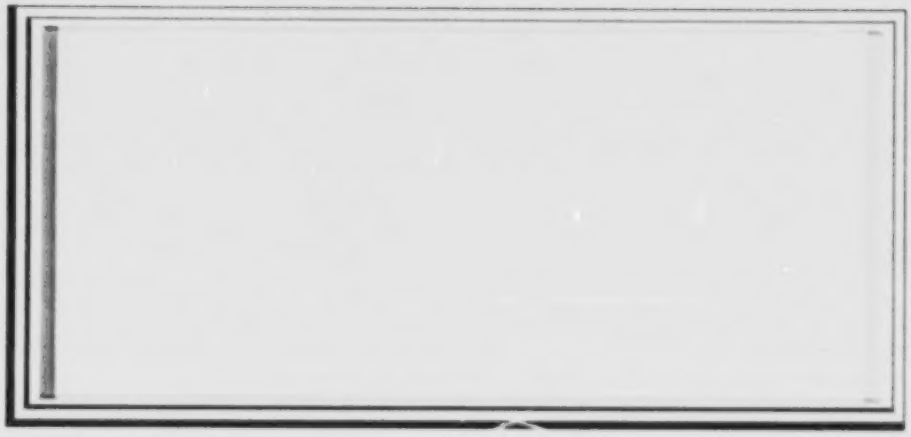

ZENON Environmental Inc.

TITLE: DEVELOPMENT OF A PROCESS FOR THE TREATMENT OF OIL/WATER/MINERAL EMULSIONS FROM IN-SITU BITUMEN/HEAVY OIL RECOVERY OPERATIONS

FINAL REPORT

Prepared by:

ZENON ENVIRONMENTAL INC.

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File No. CO854031

January 14, 1987

Dr. H. Sawatzky
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Re: **DSS CONTRACT 09SQ.23440-5-9176 CONTRACT SERIAL NO. 0SQ85-00186**
DEVELOPMENT OF A PROCESS FOR THE TREATMENT OF OIL/WATER/MINERAL EMULSIONS FROM IN-SITU BITUMEN/HEAVY OIL RECOVERY OPERATIONS

Dear Dr. Sawatzky:

Further to our telephone discussion of November 3, 1986, and to my letter dated December 12, 1986, please find enclosed, four (4) copies of the Final Report for the above project.

The final version of the report contains the amendments that were agreed to in the above correspondence.

I trust that the above meets with your approval.

If there are any questions regarding the above, please do not hesitate to contact me.

Sincerely,

Gabriel Nicolaides

Gabriel M. Nicolaides
Process Engineer

GMN/mp
Encl.
cc. Mrs. P. Green
Department of Supply & Services

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Wastewater Technology Center Personnel

A. Zaidi - Process Development Engineer

D. Averill - Process Development Engineer

D. Vachon - Physical Scientist

Canterra Energy Ltd. Personnel

J. Kowalski

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were drawn from the results obtained during the experimental program:

i) The well head produced water emulsion was very stable with respect to heating, freezing, and aging, but could be destabilized by acid addition below a pH of 4.

ii) The emulsion could be effectively destabilized and separated by gravity at ambient temperature using alum. However, at high temperature (35°C), the emulsion could be destabilized, but would not settle due to a low density difference between the oil and water phases.

iii) Glass fiber filtration produced a very clean filtrate, but the extremely low flow rates obtained would be a limiting factor in the full scale application of this process.

iv) Granular media filtration provided very high flow rates with moderate pressure drops, but the filtrate quality was not satisfactory.

v) The destabilized oil flocs trapped in the filter media during the granular media filtration runs were not dissolved by solvent addition, but were easily backwashed by water flow. The oil flocs exhibited hydrophilic behaviour due to the high water content in the flocs.

vi) The destabilized oil sludge was effectively filtered by a vacuum filtration process with the aid of a flocculant. The entrapped oil could be recovered from the filter cake by heating or by solvent extraction. The high operating costs

of this process, however, render it unsuitable for this application.

vii) Gravity belt filtration produces a clean filtrate with a suspended solids content of about 80 mg/L. The filter cake produced contains roughly 20% by weight of oil, and is suitable for recycle to the heater treater.

viii) The supernatant produced from the coagulation/flocculation process has a very low turbidity (ie. less than 5 NTU), and contains low suspended oil levels. The supernatant requires no further reduction in oil content prior to hot lime softening.

ix) The cost comparison between the proposed and conventional treatment processes indicate that the proposed process is 17% less expensive. For an average sized produced water treatment system (ie. 1000 U.S.gpm), this translates into a net savings of approximately $230,000 per year compared to the conventional treatment process. The proposed process is also better suited to handle upset conditions such as changes in feed oil content.

x) It is recommended that the proposed process be evaluated further, at pilot scale. An on-site pilot plant program would enable verification of the ability of the process to handle variations in feed oil content, on a continuous basis.

SOMMAIRE DES CONCLUSIONS ET RECOMMANDATIONS

Les conclusions suivantes ont été tirées des résultats obtenus au cours du programme expérimental:

i) L'émulsion d'eau produite à la tête de puit était très stable en ce qui concerne le réchauffement, la congélation et le vieillissement, mais pouvait être déstabilisée par un ajout d'acide d'un pH inférieur à 4.

ii) L'émulsion pouvait effectivement être déstabilisée et séparée par gravité à la température ambiante en utilisant de l'alun. Toutefois, à une température élevée (35°C), l'émulsion pouvait être déstabilisée, mais ne se déposait pas en raison de la très faible différence de densité entre les phases d'eau et d'huile.

iii) La filtration à la fibre de verre a donné un filtrat très propre, mais les débits extrêmement bas obtenus seraient un facteur limitatif lors de l'application normale de ce procédé.

iv) La filtration au moyen de granules a donné des débits très élevés et des baisses de pression modérées, mais la qualité du filtrat n'était pas satisfaisante.

v) Les flocons d'huile déstabilisés emprisonnés dans le milieu filtrant pendant les cycles de filtration, n'étaient pas dissous en ajoutant du solvant, mais furent facilement lavés à contre-courant par le débit d'eau. Les flocons d'huile ont présenté un comportement hydrophile à cause de la teneur en eau très élevée dans les flocons.

vi) Le cambouis d'huile déstabilisé fut effectivement filtré par procédé de filtrage à vide aidé d'un agent floculant. L'huile ainsi emprisonnée a pu être récupérée du gâteau du filtre par extraction thermique ou au solvant. Toutefois, les coûts élevés de ce procédé le rendent innacceptable pour cette application.

vii) La filtration gravitaire par courroie donne un filtrat propre avec une teneur en matières solides en suspension d'environ 80 mg/l. Le gâteau du filtre obtenu contient approximativement 20% de son poids en huile, et convient au recyclage par traitement thermique.

viii) Le liquide surnageant obtenu du procédé de coagulation/floculation a une turbidité très basse (c.-à-d. moins de 5 NTU) et contient de bas niveaux d'huile en suspension. Le liquide surnageant ne requiert aucune autre réduction en teneur d'huile avant l'adoucissement à chaud.

ix) La comparaison des coûts entre les procédés de traitement ordinaire et ceux proposés indique que le procédé de traitement proposé est 17% moins coûteux. Pour un système moyen de traitement de l'eau (c.-à-d. 1000 gal. am.), cela se traduit par une économie annuelle nette d'environ 230 000 $ par rapport au procédé de traitement ordinaire. En outre, le procédé proposé convient mieux pour faire face à des conditions inhabiluelles telles que les changements dans la teneur en huile.

x) Il est recommandé que le procédé proposé soit évalué davantage à l'échelle pilote. (4) l'implantation sur place d'un programme-

pilote permettrait de vérifier l'efficacité du procédé, sur une base continue, lorsque la teneur en huile varie.

1.0 INTRODUCTION

1.1 Background

The conventional treatment train employed in the processing of produced water is displayed in Figure 1-1. In this treatment train, a combination of a skim tank followed by induced gas flotation (IGF) is used for removal of the bulk of the emulsified oil present in the produced water stream. Sand filtration is used for polishing of the effluent from the IGF prior to use as boiler feed.

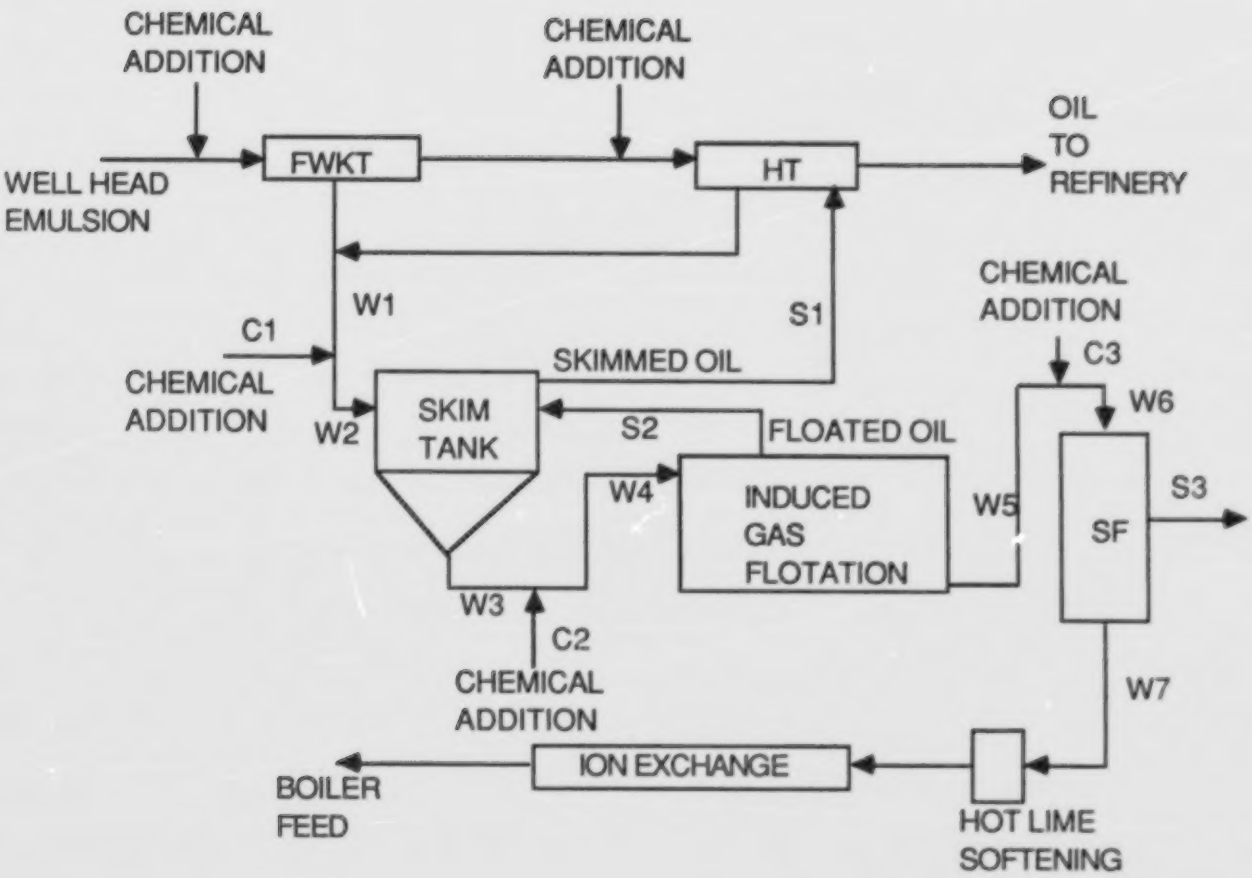
Despite its widespread acceptance and use, the conventional treatment train has high operating costs, and suffers from a number of operating problems. The high operating costs are primarily due to the need for addition of expensive, proprietary chemicals at several nodes in the system (ie. prior to the free water knock-out tank, the skim tank, induced gas flotation, and sand filtration), as well as the high energy requirements for induced gas flotation. The operating problems that have been experienced include:

i) the lack of mixing in the skim tank results in short-circuiting of the emulsion, preventing sufficient residence time for demulsification,

ii) the inability of induced gas flotation to handle upset conditions, particularly higher than average feed oil concentrations, and

iii) the inability of the sand filtration process to reduce higher than expected oil concentrations in the effluent from induced gas flotation to levels specified for boiler feed.

iv) the quality of the filtrate from sand filtration does not always meet specifications for deionization feedwater.



KEY : FWKT FREE WATER KNOCKOUT TANK
HT HEATER TREATER
SF SAND FILTER

FIGURE 1-1 CONVENTIONAL PROCESS FLOW SHEET FOR TREATMENT OF PRODUCED WATER.

An alternative method for the treatment of produced water is the destabilization of the emulsified oil by the use of multivalent cations, followed by filtration of the destabilized oil. This process is potentially superior to the conventional technology as, in addition to being operationally simple and effective for solids and oil removal, the process would use inexpensive, widely available chemicals, would provide an aqueous effluent that would require very little post treatment for boiler feed, and would recover the emulsified oil in a form suitable for refining. The contents of this report describe the results of a test program designed to evaluate the potential of the destabilization/filtration process for treatment of produced water.

1.2 Objectives

The objectives of the study were:

i) to develop and optimize the process of emulsion destabilization by multivalent inorganic cations, followed by transfer of oil onto an inert filter

ii) to develop and optimize a method of oil recovery and filter media regeneration

iii) to assess the technical and economic feasibility of treating wellhead emulsions from in-situ bitumen/heavy oil recovery operations using the developed methods.

2.0 LITERATURE SURVEY

A literature review was undertaken of both published and unpublished information on the subjects of produced water emulsion characteristics, treatment methods of well-head emulsions, destabilization of produced water emulsions, and filtration of produced water emulsions. ZENON's in-house literature and texts were first reviewed and updated. A computer-assisted literature search was conducted through the DIALOG Information Service. The search was carried out by entering key words or sequences of key words for the computer to identify publications containing relevant titles or contents. The following key words and/or combinations of key words were used:

oil-water emulsions, destabilization, separation, emulsion-breaking, coagulation, filtration, filter-media, oil-recovery.

The following data bases were searched for the key words: NTIS, CLAIMS/US Patent, Chemical Abstracts, ENVIROMT2, COMPENDEX, ENERGYLINE.

The various combinations of key words generally turned up a number of matches. Each one of these matches was then screened by examining the abstract or detailed citation to ascertain whether or not the article was, in fact, relevant to the subject at hand.

As a result of the search, information about treatment of produced water emulsions appeared to be generally lacking in technical journals except for some patents. This lack of information could be due to the fact that the oil industry, as a whole, is highly

competetive, and reluctant to publish any significant details about their operations. The information obtained from the literature survey is summarized in sections 2.1 to 2.4.

2.1 Produced Water Emulsion Characteristics

Oil-in-water emulsions produced from in-situ bitumen recovery operations are generally characterized by their high stability. The high stability of the emulsion is generally attributed to the relatively high asphaltenes and resin content of the bituminous oil. The bituminous oil is also stabilized by the presence of various water soluble surface active materials, along with fine mineral particles (Schramm, 1985).

The asphaltenes are a highly polar material and tend to form a membrane skin around the bitumen oil droplet. Alberta area heavy oils contain 10 to 20 wt.% of asphaltenes compared to about 2 wt.% in light crude oils. It has been reported that the reaction of bitumen with steam or hot water can form various water soluble surface active materials which reduce the interfacial tension between the oil and the water, resulting in highly stable emulsions. Burchfield and coworkers (1979) investigated the change of surface tension of produced water by lowering the pH and found that surface tension decreased rapidly as the pH dropped to about 4. They also observed that the surface tension increased when 0.5 wt.% of activated carbon was added to the produced water. The increase of the surface tension was a result of removal of surface active material from the produced water by adsorption onto the carbon. Gewers (1968) observed that clay colloids in the produced water attached to the surface of bitumen oil droplets

coated by asphaltenes, thus producing very stable emulsions. It was also indicated that conventional destabilization processes such as the use of destabilizing agents or electrostatic coalescence were not effective on clay-stabilized emulsions.

The properties of produced water from various sites in Alberta and the United States were well documented in the literature (CH_2M-Hill - 1981, 1982, and ZENON - 1985A, 1985B). In Table 2-1, some of the important properties of the produced water are presented.

The oil contents of well head emulsions are generally higher and wider in range compared to that of skim tank effluents because additional oil removal is achieved with the help of demulsifying chemicals in the skim tank. The soluble inorganic content of produced water is stongly dependent on the leaching properties of the oil formation matrix. The inorganic and organic acids (eg. sulphuric acid, carboxylic acids) which are formed by the reactions between bitumen and steam dissolve inorganic salts in the formation matrix. High acid and dissolved solids concentrations in the produced water often cause severe corrosion or scaling of the well pipes. The sulphate levels are less than 600 mg/L in most steam-flood produced water, but levels as high as 10,400 mg/L were reported by Parker (1984) in some fire-flood produced waters.

The properties of well head emulsions collected from the wells located in a well defined geographic pattern were examined by Parker (1984), who found that the water chemistry was dependent upon the proximity of the well to the firefront.

TABLE 2-1 EMULSION PROPERTIES

PROPERTY	EMULSION TYPE A	EMULSION TYPE B
TSO (mg/l)	96-2000	7-32500
TSS (mg/l)	68-447	27-300
TDS (mg/l)	844-31349	353-9370
PH	6.8-8.6	7.4-8.3
HARDNESS (mg/l)	41-890	13-488
SILICA (mg/l)	8-380	48-300
CALCIUM (mg/l)	48-290	3-98
SODIUM(mg/l)	215-11007	430-3400
CHLORIDE(mg/l)	119-13348	510-6300
SULPHATE(mg/l)	22-525	24-360

Note;
TSO ; TOTAL SUSPENDED OIL
TDS : TOTAL DISSOLVED SOLIDS
TSS : TOTAL SUSPENDED SOLIDS
EMULSION TYPE A : SKIM TANK EFFLUENTS
EMULSION TYPE B : WELL HEAD EMULSIONS

The temperatures of produced water from a steam injection operation typically range from 65 to 82°C. The pH of the water is in the 6.8 - 8.6 range.

The characteristics of produced water vary between wells in the same area and changes over the life time of the well operation. In steam injection recovery operations, the water quality is typically best in terms of oil content and TDS at the early stages of the production cycle, and deteriorates towards the latter stages.

The water quantity required to produce the same amount of oil increases gradually towards the latter stages of operation, because of the decreasing quantity of oil in the oil formation matrix (CH_2,M-Hill, 1982). The ratio of water to oil produced in the Cold Lake area of Alberta is typically 4:1 at the present time. Water to oil ratios as high as 10:1 have been reported from older wells in some areas of California. In Canada, the average water to oil and steam to oil ratios are projected to increase from about 4:1 in 1984 to 6:1 in the year 2000.

The expected increase in water requirement with time emphasizes the necessity of efficient and economical reuse of the produced water. Recycle and reuse of the produced water would eliminate problems associated with obtaining a source of water for steam generation, as well as disposal of the unused produced waters. These waters are not dischargeable without further treatment.

2.2 Treatment of Well-Head Emulsions

The treatment requirements of produced water depend upon the operating pressure and type of steam generation system used. A survey

of steam generation techniques which may utilize produced water found that at the present time economics still favoured the use of conventional once-through steam generators which produce 80% quality steam and require relatively low quality feedwater (CH_2M-Hill, 1982). Table 2-2 presents general oilfield requirements for boiler feedwater and other uses as obtained from the literature (CH_2M-Hill, 1981, 1982). It should be noted that essentially all oil, hardness, and suspended solids must be removed to treat produced water for use as once-through boiler feedwater. In this review, treatment processes for removing oil and suspended solids from produced water were emphasized. Further treatment processes to meet the water quality requirements for once-through boiler feedwater have been reviewed elsewhere (ZENON 1985B, CH_2M-Hill, 1981, 1982).

The American Boiler Manufacturers Association guidelines for the feedwater of once-through steam generators recommend oil removal to levels of 7 mg/L or less, with a desirable level being less than 1 mg/L. Oil concentrations above this can cause scale adherence, film boiling, and coking in the boiler, and fouling of ion exchange resins in the feedwater treatment train.

Conventional Technologies

A typical process flow sheet of in-situ steam injection operation is shown in Figure 1-1. The oil and produced water is pumped to a primary gravity separator (FWKT), where the bulk of the bitumen-rich oil phase is separated by density difference with the help of demulsifying chemicals. The bitumen-rich oil phase is a stable water-in-oil emulsion containing up to 70% of water. The oil

TABLE 2-2

WATER QUALITY REQUIREMENTS FOR BOILER FEEDWATER PREPARATION AND OTHER USES
(from CH_2M Hill, 1981)

Parameter	Once-Through Steam Generator Note 4	Thermosludge Generator Note 4	Deep Well Disposal-Note 1	Irrigation	Cooling Water Make-up
Total Hardness mg/L as $CaCO_3$	< 0.5	100-2000			NOTE 2
Silica mg/L	< 50	10-250			NOTE 2
Oil mg/L	< 1	50-1000	< 20	< 5	< 1
TDS mg/L	< 8000	1000-50000		< 1000	-
Suspended Solids mg/L	0	10-500	< 5		NOTE 3
Dissolved O_2 mg/L	< 0.04	-			-
Iron	< 0.05				

NOTE 1 - Water should be chemically compatible with formation waters.

NOTE 2 - The product of Mg as $CaCO_3$ x SiO_2 < 35000 mg/L.

The product of Ca as $CaCO_3$ x SO_4 < 500,000 mg/L.

NOTE 3 - Total suspended solids in the recirculating water 200 mg/L.

NOTE 4 - These are vendor recommendations. Some of these values have been exceeded in actual practice.

phase is commonly treated by a series of heater treaters at high temperature to remove the water and mineral content to below 0.5% BS&W. The produced water from the primary separator is often a very stable oil-in-water emulsion containing up to a few percent of oil. An above ground skim tank is the most common gravity separator used in the oil field to separate the large oil droplets with the addition of demulsifying chemicals. Suspended oil concentration of the skim tank effluent is in general below 600 mg/L if the system is properly operated (Vachon, 1986). Komak and Grisard (1980) indicated that the conventional gravity separators including skim tank and API are inherently slow and inefficient on bitumen and heavy crude oil produced waters because the oil density is very close to that of water. Furthermore, the high viscosity and surface tension of the heavy oil prevent coalescence of the oil droplets even after contact of the oil droplets has been made. The remaining fine oil droplets in the water effluent of the skim tank are commonly removed by induced gas flotation (IGF). Separation of oil droplets is promoted by gas bubbles injected to the IGF unit. The gas bubbles attach to oil droplets and solid particles, causing them to rise to the surface where the resulting froth is skimmed off. Overall performance of an IGF unit depends on variables such as oil droplet size, gas bubble diameter, liquid residence time, and polyelectrolyte dosage. Of these factors, the chemical dosage is the only one easily changed in an operating system. Sylvester et al. (1980) found that IGF was unable to effectively remove oil droplets with a diameter of 2 microns or less. The suspended oil concentrations of the water effluent from a well operated IGF unit range from 10 to 25 mg/L. Behie and coworkers

(1982) pointed out the operating problems associated with IGF. They indicated that improper design or operation of only one important element of a unit such as the air sparger can result in very poor performance even if all other elements are well designed. Other problems can be expected to be particularly acute whenever feedwater concentrations change significantly or rapidly. The relatively high energy requirement, expensive float handling procedures, and high cost of chemicals, chemical handling and storage results in high operating cost of the IGF.

Dissolved air flotation (DAF) and dissolved gas flotation are extensively used to remove the suspended solids and oils in wastewater treatment processes. However, application of DAF for treatment of produced water has been limited mainly due to the high water temperature that limits air solubility and potential equipment corrosion problems.

The water effluent of an IGF unit usually requires a polishing filtration step in order to prevent possible interference with downstream processes. Granular filters (single or multi media) have been extensively utilized in this application. Oil removal in granular filtration involves a complex mechanism of direct filtration, coalescence and adsorption onto filtered solids. Addition of chemical coagulants to the feedwater stream is commonly practiced to enhance floc formation of fine oil droplets and subsequent removal of the flocculated oil on the filter media. The problems associated with the filtration are the clogging of the filter media, and leakage of oil droplets through the filter under a certain upset condition in which the IGF unit releases water effluent with high oil concentration.

Alternative Technologies

Due to the expensive and inefficient existing treatment processes as well as potential shortage of water supplies and environmental concerns, various processes for treatment of produced water have been attempted. These include API separators, corrugated plate interceptors (CPI), chemical coagulation, coalescers, spherical agglomeration, electrolytic separation, ultrafiltration, etc.

API and CPI have been successfully utilized for gross oil removal in refinery wastewater treatment processes. These processes depend mainly on the density difference of oil and water and the coalescence of oil droplets onto an oleophilic surface. Bitumen emulsions stabilized with mineral particles, however, were not effectively separated by these methods mainly because of low density differences and small oil droplet size. Furthermore, clay stabilized oil droplets tend not to wet and coalesce onto the oleophilic surface.

Chemical coagulation has received very limited attention for treatment of emulsified oil in the heavy oil industry even though it has been the most common practice for destabilization of colloidal particles in wastewater treatment operations. In principle, chemical coagulants which are multivalent ions neutralize the opposite charges on a colloidal particle, resulting in agglomeration of the particles by attractive forces such as Van der Waals force. It has been known that acidification of produced water emulsions with acids such as sulphuric, hydrochloric, nitric, and acetic to pH values below 4.5, destabilize the emulsion, resulting in partial deoiling and precipitation (ZENON 1984A, 1985B). Lowering of the pH of the emulsion appeared to suppress the electrical double layer of the oil

droplet, causing destabilization of the emulsion (Komak, 1980). Neutralization of negative charges on the oil droplet can be effectively done with multivalent cations such as Al^{3+}, Fe^{3+}, and Ca^{2+}. ZENON (1985A) found that ferric ions leached from coal particles effectively destabilized well head emulsions obtained from Alberta. Subsequent investigation by ZENON revealed that small dosages of multivalent inorganic coagulants could destabilize the well head emulsion. The destabilized oil droplets formed flocs but did not coalesce to give a free oil phase. Furthermore, the oil flocs were broken easily by gentle agitation. Chemical coagulants have been used in the oil field as destabilizing agents for gravity separation processes such as a skim tank and IGF.

The use of various coalescers for treatment of light crude oil emulsions has been successful mainly because of good wettability of the oil droplet onto oleophilic or hydrophobic media. In a coalescer, the emulsion passes through an oleophilic medium and the oil wets and adsorbs onto the surface of the medium and gradually agglomerates. In a certain unit such as a vertical tube coalescer, once the size of oil agglomerate is large enough, it separates from the coalescing medium and rises to the surface as free oil. In other units, the saturated bed may be backwashed or compressed to remove oil or the media may be discarded. Many types of coalescing media have been used, for instance; granular polymeric resins, polymer coated sands, polyurethane foam, and other oleophilic plates.

The application of coalescers to treatment of produced water emulsion has been limited in the past by a number of factors. Conventional coalescers are designed for treatment of refinery oily

wastewaters containing negligible suspended solids and are operated in an upflow mode. The high solids levels typically present in produced water will cause severe plugging and inefficient backwashing of the media. In recent years, a number of manufacturers have developed coalescers which could avoid the problems discussed above. The Gravery Company (Union, N.J.) developed a granular resin coalescer/separator bed and carried out a number of pilot scale tests at production sites and refineries. Typical oil removal efficiencies ranging from 95% to 99% were achieved with feed oil concentrations ranging from 10 mg/L to a few thousand mg/L (O'Connel, 1983). The coalescer was operated in a down flow mode and backwashed to remove suspended solids. A coalescing unit developed by Marco (Seattle) made use of the adsorption affinity of oil onto polyurethane foam. When the foam is saturated, the oil is recovered by compressing the foam. Because the produced water emulsions from bitumen recovery are often stabilized with highly polar asphaltenes and mineral particles, the oil droplet does not easily wet the oleophilic coalescing media, and these coalescers are hence not effective for treatment of the emulsions. Another factor that has limited the application of the coalescers is that many of the coalescing media will not tolerate the high temperatures of the produced water.

Electrolytic flotation of Cold Lake produced water was investigated by Nagendran and his coworkers (1980). Although the process could effectively remove the oil droplets, the costs of chemical coagulants and electricity made the process economically impractical at a large scale. An electrolytic separator which made use of scrap iron to produce ferric ions with air sparging was

successfully utilized for treatment of light oil emulsions (Weintraub et al., 1980). In this process, the Fe^{3+} ions acted as coagulants to destabilize the emulsions resulting in flotation of the oil flocs. This process would not, however, be effective in a system where the emulsion has a low density difference or a high viscosity.

A spherical agglomeration process developed by researchers at the National Research Council of Canada has shown potential to break the produced water emulsions (Rowat 1980, Majid et al, 1985). In this process, an aqueous coal slurry was added to the produced water emulsion, and high speed mixing was applied in order to provide good contact between the oil droplets and the coal particles. The oil droplets attached and adsorbed onto the surface of the coal particles, resulting in spherical agglomeration. The adsorbed oil was recoverable from the agglomerates of oil and coal. In order to increase the heat value of high ash coal, the coal was treated with produced water emulsion by spherical agglomeration. Complete separation of oil and coal was not necessary in this application.

Ultrafiltration is basically a low pressure membrane filtration process on the molecular level by which solvent and solute molecules are separated by shape and size with some degree of influence from ionic strength and the pH of the solution. UF membranes typically have a pore size of 50 to 500 angstrom units. Ultrafiltration has been utilized in the treatment of emulsified oily wastewater from machining operations, automotive plants, and rolling mill coolants, for either the recovery of oil, or the production of water suitable for reuse. In emulsified oil separation by ultrafiltration, a varying proportion of the small surfactant

molecules may pass through the membrane, while the large oil droplets are rejected. The loss of the surfactant with water in the permeate can cause the oil/water emulsion to break, thereby releasing an oil-rich phase. Depending on the membrane affinity for oil, this may result in formation of an oily layer on the membrane surface, accompanied by a gradual decrease in permeate rate with time. However, proper cleaning of the membrane at appropriate intervals can restore product rate. Ultrafiltration has been examined for the treatment of emulsions from simulated micellar-flood wastewaters by the U.S. Department of Energy (Dubey, et al., 1981). The wastewaters studied were complex and contained oil, as well as surfactants, alcohols, and polymers that were introduced to the formation during micellar flooding. Synthetic wastewaters were prepared to simulate micellar flood water, and contained fixed levels of brine, polymer, and butanol with oil-sulphonate concentrations ranging from 400 - 3400 mg/L. Operating pressures were 20 - 40 psi (138 - 276 kPa), and temperatures ranged from 21 - 32°C. Depending on oil concentration, flux rates of cellulosic membranes ranged from 20 - 40 gal/ft^2/day after 180 minutes of operation, and the permeate was essentially free of all oils, sulphonate, and polymer. This study indicated that ultrafiltration was effective, but that further studies on actual wastewaters were necessary due to their complex and site specific characteristics. Recovery of surfactants from oilfield emulsions was patented by Baddour (1978). The patent claimed that further concentration of ultrafiltration permeates and concentrates by membrane processes resulted in an efficient and economical process for recovering surfactants for subsequent reuse in the oilfield. As

discussed in previous sections, the produced water from in-situ steam stimulation operations is highly stable due to various factors, including the presence of surfactants, both naturally occuring and those which are formed during recovery processes. Farnand and coworkers (1984) observed that the produced water emulsion breaks, implying that destabilization may occur due to surfactant or emulsifier loss into the permeate. The experiments indicated the potential for UF to break these emulsions, but found that effectiveness was dependent upon the membrane material used. The use of a continuous UF membrane process to break the produced water emulsions was carried out by researchers at Energy, Mines and Resources, who identified a polar material in the permeate which was believed to be the stabilizing agent. The main concern of the process was membrane fouling, which was related to the membrane material that was employed (Farnand & Sawatzky, 1984).

In a recent study by ZENON (1986), it was found that the flow characteristics of the emulsion at the membrane surface greatly affected fouling tendencies, and that turbulent flow at the membrane significantly reduced surface fouling.

2.3 Destabilization of Produced Water Emulsions

The oil droplets of produced water emulsions generally are negatively charged and have high zeta potential, resulting in stable suspension of the droplets due to their repulsive forces. The negative charges on the oil droplets can be neutralized by adding multivalent cations or by lowering the pH of the emulsion. The neutralized droplets tend to agglomerate and form oil flocs mainly due

to attractive forces. Most light crude oil droplets coalesce to form bigger droplets when destabilized, resulting in phase separation. However, the oil droplets of the produced water emulsions generated by in-situ steam injection operation appeared not to coalesce when contacted even though the negative charges were neutralized. This extreme stability of the emulsion might be attributed to the protective coating of the oil droplet by the highly polar asphaltenes and resins, as well as adsorption of mineral colloids onto the surface of the oil droplet. This type of emulsion could be destabilized by the following methods or combination of methods; acidification, coagulation, surfactant removal from the water, or chemical demulsification.

ZENON, (1985A, 1985B) observed that the produced water collected from various sites in the Alberta area were destabilized by lowering the pH of the water below 4 and found that multivalent cations such as Al^{3+} and Fe^{3+} could effectively destabilize the emulsions. It was also noted that the destabilized oil droplets formed flocs which were easily broken and resuspended by gentle agitation. ZENON (1985A) observed that charge neutralization resulted in flocculation of the oil droplets but that the protective coating of the droplet prevented coalescence.

Farnand (1981) studied the effect of liquid polar compounds on heavy oil emulsions (W/O) with the assumption that highly polar and resin fractions relatively enriched in heteroatoms (oxygen, nitrogen, and sulphur) formed films at the water-oil interface which stabilized the emulsions. The emulsions were treated with polar compounds of many different types in an attempt to disrupt the film forming

materials by interfering with the intermolecular association including hydrogen bonding between asphaltene - asphaltene and asphaltene - resin fractions and/or by competing at the interfaces with the asphaltenes and resins. The polar additives used varied considerably on molecular weight range and contained oxygen, nitrogen, and sulphur heteroatoms in the form of different types of functional groups. Among the chemicals tested, it was found that aliphatic acids, alcohols, and ketones with a molecular weight of 80 to 250 were the most effective demulsifying chemicals.

McCoy et al (1982) patented a process for breaking bituminous emulsions using water soluble demulsifiers consisting of ethylene oxide and propylene oxide polymers having molecular weights greater than about 10,000 at temperatures between 25 and 120°C. Detailed destabilization mechanisms of the emulsions were not disclosed. Several other patents for treating the heavy oil emulsions with high molecular weight ethylene oxides with the optional addition of alkali earth metals were issued (Mahendra et al, 1977, Bialek, 1981). Polymeric demulsifying chemicals commonly used for bitumen emulsions are either polyalkylene oxides, polyesters having high molecular weight (about 10^6 mol.wt.), or other molecules containing large hydrophobic or hydrophilic portions.

Heating of the emulsion reduces the oil viscosity, increases particle motion, alters relative fluid densities, and reduces boundary strength around the emulsified droplet. Demulsifying chemicals can be better dispersed into the oil droplets at higher temperatures.

2.4 Filtration and Oil Recovery

Filtration has been one of the most common means for removal of small suspended solids from water and wastewater streams. In the oil field, granular media filtration is used as a polishing step for treatment of oil-in-water emulsions having low suspended oil content, typically less than 500 mg/L. Granular media which have been used in oily wastewater treatment include sand, crushed anthracite coal, diatomaceous earth, powdered or granular carbon, and coconut shells. These media have been used either singly or in combination, depending on the characteristics of the water. The mechanisms involved in removal of suspended matter by a granular filter are very complex. The dominant mechanisms depend on the physical and chemical characteristics of the water (O'Melia and Stumm, 1967). With deep granular filters of coarse material, removal is primarily within the filter bed. Some solids may be removed by the simple mechanical process of interstitial straining. Removal of other solids, particularly the smaller ones, depends on two types of mechanisms. First, the small particle must be transported from the bulk of the fluid within the interstices to a position close to the surface of the media. Transport mechanisms may include gravitational settling, diffusion, interception, and hydrodynamics; these mechanisms are affected by physical characteristics such as size of the filter medium, filtration rate, fluid temperature, and the density and size of the suspended particles. Second, as the particle approaches the surface of the medium, or previously deposited solids on the medium, an attachment mechanism is required to retain the particle. The attachment mechanisms may involve electrostatic interactions, chemical

bridging, or specific adsorption, all of which are affected by the coagulant applied in the pretreatment and the chemical characteristics of the water and the filter medium.

Granular filtration is a cyclic process. The filter is washed to restore its capacity when the effluent quality becomes unacceptable, or when the pressure drop through the filter reaches a predetermined value. For gravity filters, the terminal head loss selected is usually the actual head available; operation beyond this point results in an inability to maintain the desired filtration rate. The filter is usually washed by reversing the flow of water through the filter at a rate adequate to lift the grains of filter medium into suspension, that is, the rising water causes expansion of the filter medium. The deposited material is thus flushed up through the expanded bed and to waste through the wash water gutters.

Single or dual media filters were installed downstream of induced gas flotation units for the removal of the remaining fine oil droplets from the IGF effluent. Addition of chemical coagulants and/or flocculants prior to the filter inlet has been a common practice in order to increase filtration efficiency. The chemicals destabilize the emulsion and enhance floc formation.

Humenick and Davis (1978) investigated high rate filtration of refinery oily wastewater emulsions. A synthetic wastewater consisting of oil and fine clay particles was used to simulate actual wastewater emulsions. The filtration efficiency in terms of oil removal, suspended solids removal, and pressure drop was examined with the operating parameters such as influent oil and suspended solids concentrations, filtration rate, chemical filter aid, and oil types.

The experiments indicated that high rate filtration of the solid stabilized oil-in-water emulsions with a dual media filter of anthracite and sand was not practical without the addition of chemical filter aids. It was also noted that solid-oil emulsion droplets remained intact regardless of whether or not they were being removed by the filter, or if they passed through the filter media. No separation of the stabilized clay solids from the oil droplets was observed. Removal in the filter was proposed to be accomplished primarily by the entrapment of the emulsion particles in the three-dimensional polyelectrolyte complexes and the subsequent capture of these larger floc particles in the filter media pores. This mechanism could explain the inefficient separation of produced water emulsions stabilized with mineral particles by sand filters or other coalescing filters.

Researchers at the Wastewater Technology Centre (Burlington, Ontario) have conducted extensive granular filtration runs with synthetic bitumen emulsions. A pilot scale sand filter has been operated under various operating conditions in order to maximize filtration efficiency. Chemical coagulants to be tested in the filter were screened by coagulation tests via a modified Ives' filterability test unit. Ten to twenty percent of the optimum coagulant dosage determined by coagulation test was recommended to be added in-line prior to the filter feed inlet. Inorganic coagulants such as alum and ferric chloride proved to be effective for destabilization of the bitumen oil emulsions. It was observed that the destabilized oil flocs did not properly wet the filter media (sand, anthracite), and that the flocs could be easily backwashed by water.

A preliminary investigation of glass wool bed filtration with produced water emulsion was carried out by ZENON (1985A). Clean filtrate was obtained, but the effectiveness of the filtration was limited by a high pressure build-up and a limited flow rate. The oil flocs trapped in the filter media were recovered by a solvent.

In general, the use of granular or fiber-bed filters as a polishing step has been relatively successful for treatment and removal of residual emulsified oil in the oil field. At high oil concentrations, however, rapid pressure build-up, frequent backwashing, and large backwash water requirements make the use of filtration impractical on a large scale.

3.0 EXPERIMENTAL PROCEDURES

3.1 Characterization of the Emulsion Sample

3.1.1 Sample Preparation

Two 45 gallon drums of well head emulsion were obtained from Canterra Energy's in-situ heavy oil recovery project at Meota, Saskatchewan during the month of December, 1985. Each drum contained a layer of settled heavy oil, a layer of floating oil, and a middle layer of stable oil-in-water emulsion. When the drums were opened, the samples emitted a strong hydrogen sulfide odour. The floating oil layers from each of the drums were skimmed off and the oil-in-water emulsions were poured into a 1000 L polyethylene tank. The composite emulsion was mixed for several hours and transferred to two clean 45 gallon drums for use throughout the experiments. The composite emulsion was essentially free of floating oil and settled heavy oil, and was considered to be roughly equivalent to the effluent of a primary oil separation tank used in oil field operations. In order to ensure that a representative sample was taken from the composite sample in the drums, the emulsion was well mixed prior to sampling for analysis or for experimental use.

3.1.2 Stability of the Oil-in-Water Emulsion

The stability of the produced water emulsion was investigated by examining the effect of heating, freezing, acid addition, and aging on emulsion stability.

Effect of Acid Addition

Five 50 mL samples of the emulsion were prepared in 250 mL Erlenmeyer flasks. The pH of four of the samples was adjusted via addition of sulphuric acid. The pH values tested were as follows: 2, 3, 4, and 5. The fifth sample was used as a reference.

The samples were well mixed and allowed to stand for 24 hours at room temperature (20 $\pm$ 1°C). The characteristics of the samples were visually observed and compared with the reference sample in terms of floc formation, settling properties, and supernatant quality.

Effect of Temperature

The effect of temperature on the stability of the emulsion sample was examined at two different conditions (ie. heating and freezing). A 50 mL aliquot of the emulsion in a polyethylene bottle was heated in a boiling water bath for a 30 minute period of time. The sample was then allowed to cool down to 20°C.

A second 50 mL aliquot of emulsion was placed in a polyethylene bottle and put in a freezer maintaining a temperature of -10°C for 24 hours. The frozen sample was removed from the freezer and allowed to warm up to 20°C. The characteristics of the samples were visually observed in terms of floc formation and supernatant quality.

Effect of Aging

A sample of the emulsion was kept at ambient temperature (20°C) for a period of three months. At the end of this time, a

subsample was withdrawn and analyzed for the following parameters: pH, turbidity, conductivity, total dissolved solids, total suspended solids, and total suspended oil. Protocols used for analysis are provided in Appendix A. The analytical results were compared with those obtained on the fresh sample, to determine the effect of aging on emulsion properties.

3.1.3 Analysis of the Chemical Properties of the Emulsion

At the start of the test program, a representative sample of the emulsion was taken and analyzed for the following parameters:

- pH
- Conductivity
- Turbidity
- Total Suspended Solids (TSS)
- Total Suspended Oil (TSO)
- Total Dissolved Solids (TDS)
- Total Dissolved Oil (TDO)
- Alkalinity
- Filtered Organic Carbon (FOC)
- Organic Acids
- Anion Scan
- Cation Scan
- Hardness (by calculation)
- Titration Curve

The FOC, anion scan, and cation scan were performed on samples which had been filtered (0.45 micron) prior to analysis. The procedures used for these analyses are presented in Appendix A.

3.2 Destabilization of the Emulsion

Three different approaches were used for chemical destabilization of the emulsion:

i) acid addition

ii) use of inorganic coagulants

iii) use of inorganic coagulants in combination with a flocculant aid.

The procedure that was employed for acid addition was described previously in Section 3.1.2. Sections 3.2.1 and 3.2.2 outline the procedures that were used to evaluate coagulation and coagulation/flocculation.

3.2.1 Coagulation

The inorganic coagulants that were evaluated during the test program were as follows: alum, ferric chloride, prepolymerized aluminum, and prepolymerized iron. A description of these coagulants and the destabilization mechanism is given in Section 2.3. The procedures used for coagulant preparation are provided in Appendix B.

Standard jar tests were conducted on each of the four inorganic coagulants to determine which coagulant was most effective for emulsion destabilization. For these tests, a total of six jars were prepared for each coagulant type. One of the jars was a blank

which served as a reference, the remaining jars were subjected to various coagulant and pH dosage conditions.

During these tests, the following coagulant dosages were evaluated: 3.0, 5.0, and 10.0 mmol/L as the metal ion. The 3.0 and 10.0 mmol/L dosages were evaluated at one pH level, the 5.0 mmol/L dosage was evaluated at three pH levels. For the aluminum-based coagulants, the pH levels that were investigtated were 6.0, 6.5, and 7.0; for the iron-based coagulants the pH was adjusted to values of 5.0, 5.5, and 6.0. These values were chosen in order to correspond with the minimum solubility conditions for aluminum and iron.

The procedure that was employed for the jar tests is given in Appendix C. During the jar tests, the results were monitored for floc formation, settling velocity, and final sludge height. At the end of each test, samples of the supernatant were withdrawn and analyzed for pH, conductivity, and turbidity. The turbidity values were compared to determine which of the coagulants and which of the conditions tested was most effective for emulsion destabilization.

A further set of jar tests were conducted on the coagulant which gave the best results, in order to optimize the pH and coagulant dosage conditions. These conditions were then evaluated at 35°C, in order to determine the effect of elevated temperature on the settling properties of the destabilized emulsion.

3.2.2 Coagulation/Flocculation

An additional set of jar tests were conducted using a flocculant aid in combination with the best inorganic coagulant, as determined in Section 3.2.1. Due to its recent success in a similar

oil field application (Vachon, 1986), Percol 728 was selected as the flocculant aid. Percol 728 is a cationic sodium acrylamide-based copolymer with a molecular weight of approximately seventeen (17) million daltons. The Percol 728 was tested at dosages of 1, 5, and 10 mg/L, in conjunction with coagulant dosages of 0.45 and 3.0 mmol/L. The jar tests were monitored for settling rate, floc properties, final sludge volume, and supernatant quality (ie. pH, turbidity, conductivity).

3.3 Filtration and Oil Recovery

3.3.1 Filtration Experiments

A total of four different filtration processes were studied to determine their ability to trap the destabilized oil flocs. The four processes studied were glass fiber bed filtration, granular media filtration, leaf vacuum filtration, and gravity belt filtration. The procedures that were followed during the experimental program are given in Appendix D.

3.3.2 Oil Recovery

The following processes were studied to determine their ability to recover separated oil: water backwash, solvent extraction, and chemical addition (ie. tall oil, 4-heptanone). More detailed information on these recovery techniques is provided in Section 2.4. The procedures that were followed during the experimental program are given in Appendix E.

4.0 RESULTS AND DISCUSSION

4.1 Characteristics of the Produced Water

Two 45 gallon drums of well head emulsion obtained from Meota, Saskatchewan were separated by gravity and composited. The chemical properties and stability of the produced water were investigated.

4.1.1 Stability of the Emulsion

Effect of Temperature

The effect of temperature on emulsion stability was assessed at two conditions; heating and freezing. The emulsion sample that was heated to 100°C for 0.5 hour was observed to be stable. Phase separation or floc formation was not visually observed. This result is similar to those reported by others (ZENON, 1984A, 1985B). When a sample of the emulsion was frozen and thawed, the emulsion appeared to be stable, despite the presence of small quantities of separated free oil on the surface of the sample. The emulsion appeared to be more stable against freezing than the other well head emulsions that were previously examined.

Effect of pH

The effect of pH on emulsion stability was determined by acidification of the sample with sulphuric acid. Four pH levels (2, 3, 4, and 5) were investigated. The samples below pH 4 showed floc formation, with the flocs floating to the surface. The separated samples were turbid and milky. It should be noted that the destabilized oil flocs did not coalesce to yield a free oil phase, and

were easily broken apart by gentle agitation. The sample at pH 5 showed no signs of destabilization. Similar results for destabilization of produced water emulsions by acidification were reported by others (ZENON 1985A, 1985B, Burchfield et al., 1979).

The destabilization of the emulsion by acidification may be attributed to one of the following mechanisms:

i) depression of the repulsive forces between the negatively charged oil droplets

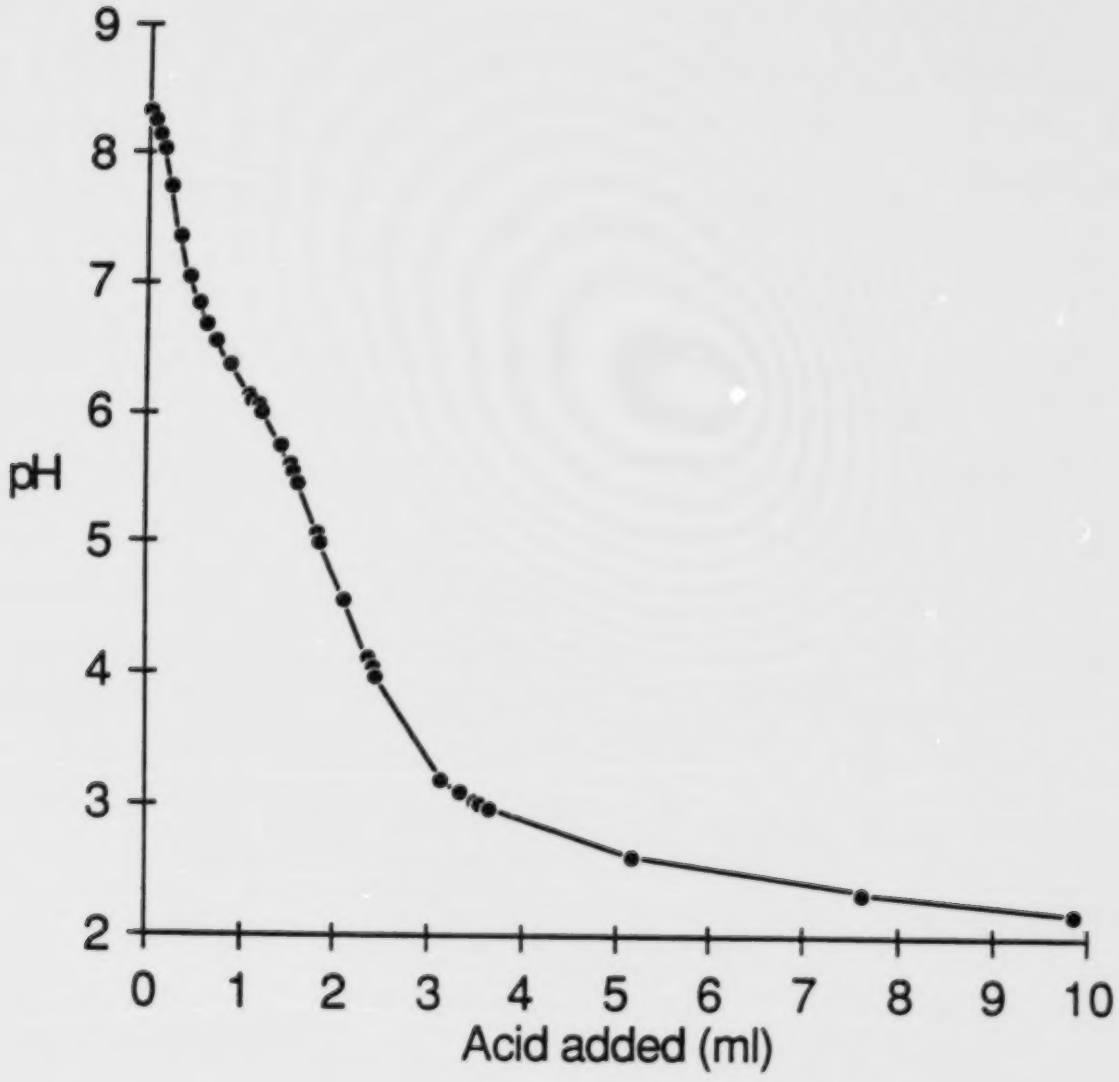
ii) inactivation of the surface active materials in the emulsion thereby increasing the surface tension of the solution

The change of pH with incremental addition of acid for a 100 mL sample was monitored and plotted in Figure 4-1. The initial pH of the emulsion was about 8.4 and dropped quickly to a value of about 3 after addition of 3 mL of 0.1 N H_2SO_4 solution. The pH of the emulsion slowly decreased upon further addition of titrant.

The characteristics of the titration curve that was obtained for the emulsion was not similar to that which is obtained for solutions which contain only the bicarbonate ion. Titration curves for bicarbonate-containing solutions are characterized by a sharp initial break with an end-point in the vicinity of pH 4.2. The curve that was obtained reflected the co-titration of the organic acids present in the emulsion with the bicarbonate ion.

pH titration curves of various well head emulsions obtained by Parker (1984) showed a similar pattern; a poorly defined break and a distorted curve. It was found that the titration curves of well head emulsions with high sulphate levels showed similar distorted

FIGURE 4-1
pH TITRATION CURVE



patterns. The presence of short chain carboxylic acids in the emulsions was indirectly indicated by the distorted pH titration curve (Wiley, L.M. et al., 1976). This titration curve was used to calculate the alkalinity of the emulsion sample.

Effect of Aging

Since all of the experiments with the produced water sample were carried out over a period of several months after the sample was collected and shipped to ZENON, it was necessary to examine the effect of aging on the key properties of the emulsion. The produced water sample was stored at room temperature for a period of three months. The properties of the sample were analyzed at the end of this time and are compared with those of the initial sample in Table 4-1. The pH of the produced water dropped from 8.48 to 7.41. It appeared that the emulsion was stable during the storage period.

4.1.2 Chemical Properties of the Emulsion

Results of the analysis of the produced water emulsion are summarized in Table 4-2 along with those of produced water samples analyzed previously. The suspended oil concentration of the Meota sample was measured as 7107 mg/L, which is within the concentration range of typical well head emulsions. The Meota sample has slightly higher total dissolved solids (2398 mg/L) and chloride (1730 mg/L) levels than the other samples shown in Table 4-2, but the levels are still within the concentration ranges found in typical produced waters. As discussed earlier in Section 4.1.1, the relatively high

TABLE 4-1 EFFECT OF AGING ON EMULSION PROPERTIES

Emulsion Property	Initial Sample	Aged Sample
pH	8.48	7.41
TSS (mg/L)	7205	7275
TSO (mg/L)	7107	7175
TDS (mg/L)	2398	2000
Turbidity (NTU)	6800	6375
Conductivity(umho)	2440	2607

Notes;
TSS; Total Suspended Solids
TSO; Total Suspended Oil
TDS; Total Dissolved Solids

TABLE 4-2 COMPARISON OF PRODUCED WATER CHARACTERISTICS

CHARACTERISTIC	THIS WORK	SRC	EMR 1	EMRM 1	EMRM 2
FREEZING STABILITY	YES		NO	NO	NO
HEATING STABILITY	YES		YES	YES	YES
pH STABILITY	>4.0		>3.5	>4.0	>4.0
AGING STABILITY	YES			YES	
TURBIDITY (NTU)	6800			1150	6700
FOC (mg/l)	48		466	260	103
TDO (mg/l)	192			124	276.7
TSO (mg/l)	7107	24600	32500	1580	1738
TSS (mg/l)	7205		300	40	52
TDS (mg/l)	2398		518	716	2205
pH	8.48	7.06	7.65	8.01	7.96
HARDNESS (mg/l)	21.9	<0.4	19.3	3.93	79.37
ALKALINITY (mg/l)	113	122			
ORGANIC ACIDS (mg/l)	101			60	70
SILICA (mg/l)			300	100	84
CALCIUM (mg/l)	5.3	0.06	504	1.16	20
MAGNESIUM (mg/l)	2.1	0.04	1.16	0.25	7.15
IRON (mg/l)	1.33	0.06	0.6	7.92	0.57
SODIUM (mg/l)	600	426		245	640
POTASSIUM (mg/l)	64	39		6	64
CHLORIDE (mg/l)	1730	574		142	850
SULPHATE (mg/l)	107	43.5		66.7	360
ALUMINUM (mg/l)	1.1				0.33

TSO ; TOTAL SUSPENDED OIL
FOC ; FILTERED ORGANIC CARBON
TDO ; TOTAL DISSOLVED OIL
TDS ; TOTAL DISSOLVED SOLIDS
TSS ; TOTAL SUSPENDED SOLIDS
NOTE : organic acid content was determined via method outlined in appendix A

SRC SAMPLE : MEOTA, SASKATCHEWAN (APRIL, 1985)
EMR1 SAMPLE : FORT McMURRAY, ALBERTA
EMRM1 SAMPLE : FORT McMURRAY, ALBERTA
EMRM2 SAMPLE : LONE ROCK, ALBERTA

organic acid concentration in the sample (101 mg/L) might explain the distorted shape of the pH titration curve for the emulsion.

4.2 Destabilization of the Emulsion

4.2.1 Screening of the Coagulants by Jar Test

The jar test results are presented in Table 4-3. All of the coagulants exhibited a good ability to destabilize the emulsified oil, as reflected in the low turbidity values of the supernatants. All of the supernatant turbidity values were less than 4.4 NTU except for the jar with 10 mg/L of prepolymerized iron (PPI). In general, the oil flocs formed by reaction with the ferric ion were bigger than those formed with the aluminum ion. The final sludge volumes of alum and polyaluminum chloride (PAC) were about 10% higher than those of ferric chloride and PPI.

Alum was selected as the best destabilizing agent of the coagulants tested because it consistently yielded supernatants with lower turbidity. For this reason, a further optimization of alum dosage was conducted, at the following dosage levels: 0.10, 0.20, 0.30, 0.45, and 3.0 mmol/L as the aluminum ion. The results of this optimization are described below:

i) The 0.10, 0.20, and 0.30 mmol/L dosages were found to be ineffective for emulsion destabilization.

ii) The 0.45 and 3.0 mmol/L dosages were found to be effective for emulsion destabilization, producing supernatants with turbidities of 8.20 and 1.20 NTU respectively.

TABLE 4-3 RESULTS OF COAGULANT SCREENING TESTS

COAGULANT	DOSAGE mMol/L	PH	TURBIDITY NTU	SLUDGE VOL %
ALUM	3	6.68	0.8	37.8
	5	6.15	0.68	39.4
	5	6.62	0.9	37.8
	5	6.51	2.4	46.5
	10	7.19	1.4	35.4
FERRIC CHLORIDE	3	5.2	2.8	24.4
	5	4.6	2.2	26.8
	5	5.26	3.8	24.4
	5	5.93	3.2	29.9
	10	5.16	2.5	23.6
P.A.C.	3	6.91	1.1	41
	5	6.78	1.7	40
	5	6.82	1.5	42
	5	6.82	1.1	38.4
	10	6.6	4.4	53
P.P.I.	3	6.1	2.2	36.3
	5	5.87	1.2	29.1
	5	5.25	1.35	32.3
	5	6.53	1.6	25.2
	10	6.41	26	25.2

Notes;

P.A.C. : PREPOLYMERIZED ALUMINUM CHLORIDE
P.P.I. : PREPOLYMERIZED IRON
COAGULANT DOSAGES ARE BASED ON METAL ION CONCENTRATION

The 0.45 mmol/L dosage was selected as the optimum condition for emulsion destabilization, as a high quality supernatant was produced at a considerably lower chemical cost than for the 3.0 mmol/L dosage condition.

The effect of elevated temperature on emulsion destabilization was determined by carrying out jar tests at 35°C. A hot plate was used to raise the temperature of the emulsion to 35°C. After the temperature had been attained, alum was added to two separate jars at dosage levels of 0.45 and 3.0 mmol/L as Al^{3+} respectively. In both cases, flocs formed but did not settle due to the convection currents present in the sample. Since this approach was not successful, all further testing and evaluation was conducted at ambient temperature.

A sample of the supernatant generated from the 0.45 mmol/L alum jar test was subjected to analysis for boiler feedwater parameters. The results of the analyses are shown in Table 4-4.

The analysis results show that the supernatant meets the boiler feedwater requirements for silica and total dissolved solids, but that further reduction of hardness and iron are required. Although analysis for oil and grease was not undertaken due to sample limitations, it was possible to estimate the total suspended oil content in the supernatant by diluting samples of the untreated emulsion and measuring the turbidity as a function of sample dilution. A correlation was then made between total suspended oil and turbidity (see Table 4-5), which enabled estimation of the TSO level in the supernatant by measuring its turbidity and correlating the result to total suspended oil. By using this technique, it was estimated that

TABLE 4-4 RESULTS OF ANALYSES ON SUPERNATANT FROM ALUM JAR TEST

PARAMETER	JAR TEST SUPERNATANT	*ONCE-THROUGH STEAM GENERATOR
Calcium (mg/l)	5.1	N/A
Magnesium (mg/l)	2.0	N/A
Total Hardness (mg/l as CaCO3)	21.0	<0.5
Iron (mg/l)	0.15	<0.05
Silica (mg/l)	12.0	<50.0
Total Organic Carbon (mg/l)	35.0	N/A
Oil (mg/l)	see note 3	<1.0
Total Dissolved Solids (mg/l)	2,700	<8,000

Notes:

1) *Water quality requirements for once-through steam generators (see Table 2-2).
2) N/A : not applicable.
3) analysis for oil and grease was not possible due to sample limitations.

Table 4-5

RELATIONSHIP BETWEEN TURBIDITY AND TOTAL SUSPENDED OIL CONTENT IN THE EMULSION

DILUTION FACTOR	ESTIMATED T.S.O* (mg/L)	TURBIDITY (NTU)
14.2 : 1	500	750
20.3 : 1	350	615
35.5 : 1	200	290
100 : 1	71	68
250 : 1	28	26
500 : 1	14	12.5
1000 : 1	7	6.5
2000 : 1	3.5	3.5

* T.S.O. (mg/L) estimated on the basis that the raw sample had an average T.S.O. value of 7107 mg/L.

the supernatant contained a total suspended oil content of approximately 5 mg/L (ie. corresponding to a turbidity of about 4 NTU). Oil levels in this range are easily handled by the hot lime softening process.

In addition, analysis on the supernatant was conducted for the aluminum ion. It was found that the supernatant contained only 0.28 mg/L of aluminum, which was down 75% from the 1.1 mg/L detected in the raw emulsion. The reduced aluminum content in the supernatant was due to the lower solubulity of aluminum at the pH at which the jar test was conducted.

4.2.2 Coagulation/Flocculation

A set of six jar tests were conducted to determine the ability of a flocculant aid to enhance the emulsion destabilization and settling process. Percol 728 was used at dosages of 1,5, and 10 mg/L, in conjunction with alum dosages of 0.45 and 3.0 mmol/L. The results of the coagulation/flocculation tests are shown in Table 4-6.

The experimental data indicates that distinctly different results are produced from the two alum dosage levels. The lower dosage level (0.45 mmol/L) produces a supernatant with a turbidity in the 2.55 to 3.70 range, and a final sludge volume ranging from 24 to 31%. The higher alum dosage level (3.0 mmol/L) produces a turbidity in the 1.25 to 2.75 range, and a final sludge volume of 32 to 33%. In both cases, the addition of a flocculant aid resulted in the production of a denser and more coherent floc than with coagulant addition alone. This is reflected in the lower sludge volumes that were generated in the coagulation/flocculation process. The optimum

TABLE 4-6 RESULTS OF COAGULATION/FLOCCULATION TESTS

Alum Dosage (mmol/L)	0.45	0.45	0.45	3.00	3.00	3.00
Percol 728 Dosage (mg/l)	1.0	5.0	10.0	1.0	5.0	10.0
	SETTLING VELOCITY DATA					
Time (minutes)	Distance Settled					
5	1.1	5.4	7.2	0.6	2.1	4.6
10	4.4	7.0	7.9	1.1	3.9	6.1
15	6.4	7.7	8.4	2.6	5.4	7.1
20	7.0	8.0	8.5	3.6	5.9	7.4
25	7.2	8.1	8.5	4.1	6.2	7.4
1020	9.4	8.8	8.9	8.5	8.3	8.6
	SLUDGE DATA					
Height (cm)	3.0	3.4	4.0	4.1	4.1	4.0
Volume (%)	24	28	31	33	33	32
	SUPERNATANT QUALITY					
pH	7.00	6.89	6.93	6.04	5.97	5.99
Turbidity (NTU)	2.55	3.20	3.70	1.25	1.40	2.75
Conductivity (umho)	2.90	2.93	2.92	3.43	3.26	3.29

condition for coagulation/flocculation as determined from test results was 0.45 mmol/L of Al^{3+} and 1 mg/L of Percol 728. These conditions were used for further experimental work and in the techno-economic assessment in Chapter 5.0.

4.2.3 Settling Properties of the Destabilized Emulsion

During the coagulant jar tests, the floc formation and settling characteristics of the oil flocs were observed. During the coagulation process, destabilized oil droplets were bridged with the aid of the hydroxide precipitate of the corresponding trivalent cation. The hydroxide precipitates are gelatineous materials with large surface areas. The precipitates enmesh the destabilized oil droplets, and make the oil flocs settle as a blanket, maintaining the same relative position with respect to each other. This phenomenon is known as hindered settling. During the jar tests, this phenomenon was observed. As the flocs settled, a relatively clear layer of water was produced above the blanket of flocs. As settling continued, a compressed layer of oil flocs began to form on the bottom of the jar. The oil flocs in this compression zone formed a structure in which there was close physical contact between the flocs.

The settling rate of the flocs was determined by measuring the level of the supernatant/floc interface at different time intervals. The settling rate is dependent on variables such as coagulant dosage, suspended solids concentration, floc size, and pH. The size of a clarifier or a thickener is generally determined based on the settling rate of the flocs.

Figure 4-2 shows a typical settling curve for a jar test with alum coagulant. The flocs were observed to settle slowly at the beginning of the test, with the settling rate increasing to a constant value of 0.23 cm/min after 30 minutes. After the constant settling rate period, the settling rate was observed to decrease, due to compression of the oil flocs. A total of approximately 60 minutes was required to reach the final sludge height. The average settling rate during the test was 0.12 cm/min. The settling properties of alum destabilized emulsion agreed with those that were previously reported (ZENON, 1985A).

4.3 Filtration and Oil Recovery

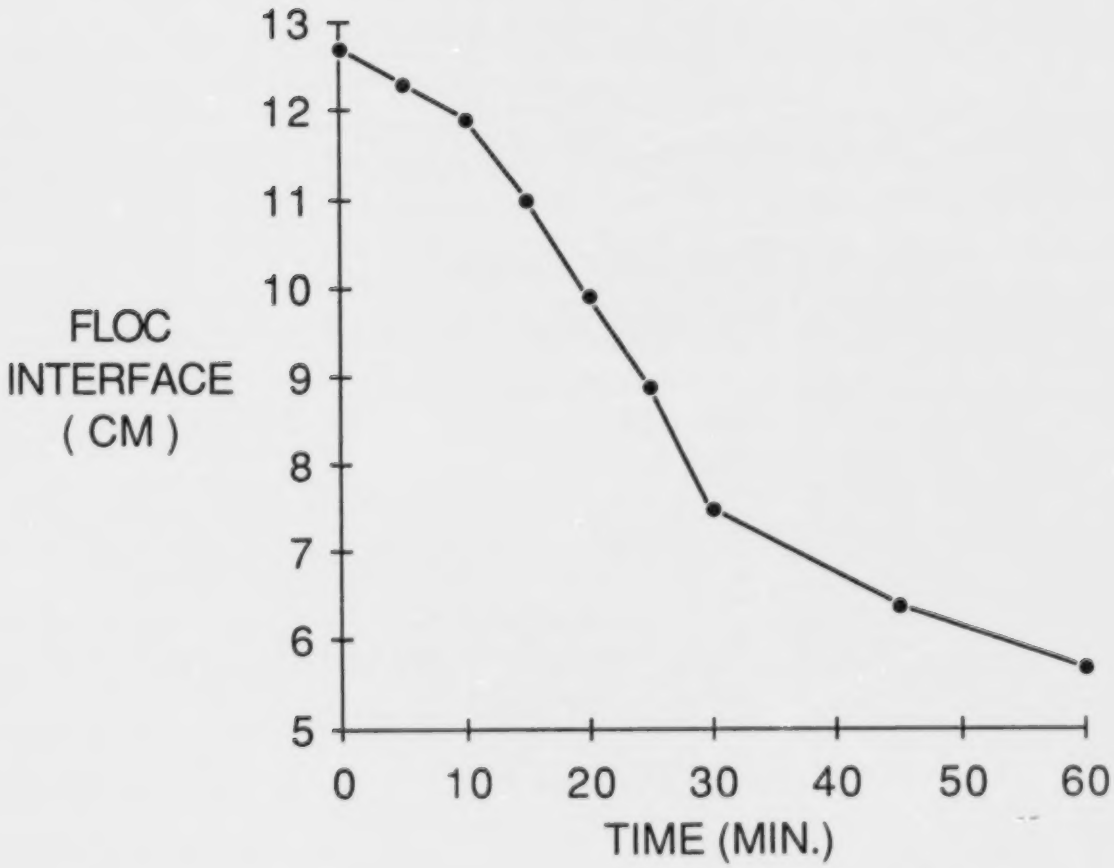
4.3.1 Glass Fiber Bed Filtration

Filtration of destabilized emulsion was conducted in a glass fiber packed column with a packing density of 0.12 g/cm^3. The produced water emulsion was destabilzed with 3 mmol/L of alum and fed to the top of the column. Pressure drops, filtrate flow rate, and filtrate turbidity were measured at predetermined time intervals.

During the test, it was observed that the filtrate flow rate decreased slowly from an initial value of 32 mL/min to a value of 2.5 mL/min after 30 minutes of run time. The filtrate was extremely clean with a turbidity of less than 1.0 NTU during the first 10 minutes of the run. The turbidity of the filtrate was measured as 1.7 NTU after 30 minutes of run time.

The destabilized oil flocs were unable to penetrate the glass fiber bed beyond a depth of 2 cm. The remainder of the bed did not come into contact with the oil flocs. As filtration proceeded,

FIGURE 4-2 TYPICAL SETTLING CURVE OF A JAR TEST



the oil flocs accumulated on the top surface of the glass fiber bed resulting in a very slow filtration rate.

Once the filtration was complete, the column was drained and a solvent was fed to the column at a flow rate of 10 mL/min. in order to recover the oil. The first 50 mL of solvent that passed through the column appeared to contain some dissolved oil. The remainder of solvent passed was observed to contain little oil. The solvent used was effective in dissolving the entrapped oil. The poor oil recovery from the glass fiber bed using the solvent could be due to the fact that the destabilized oil droplets would not coalesce to give a free oil phase. It was expected that the destabilized oil droplets were separated by thin water layers, which prevented the solvent from penetrating the water layer and dissolving the oil.

In a similar filtration of destabilized produced water emulsion using a glass fiber packed column, about 75% of the oil trapped in the filter media was recovered by passing a solvent under pressure (ZENON, 1985A). A 2.54 cm diameter filter column was packed with the glass fiber, to give a packing density of 0.20 g/cm^3. This packing density was about 70% greater than that used in the present study. The initial flow rate was 3 mL/min and the final filtration rate was less than 0.5 mL/min, probably due to the compact packing of the glass fiber.

4.3.2 Granular Media Filtration

Three different types of granular filter media (sand, anthracite, Klensorb) were tested in order to investigate their filtration performance. In the preliminary filtration runs with sand,

the coagulant dosages were varied from 15% to 100% of the optimum alum dosage determined by jar test. It was observed that the lower dosages (15% and 30%) were not effective for emulsion destabilization. The optimum alum dosage was used for further filtration runs in order to avoid the effects of coagulant dosage on the performance of filter media.

Two blank filtration runs were carried out for each filter media type; one with tap water, and a second with raw emulsion. The results of the blank filtration runs are presented in Tables 4-7 and 4-8. There were no significant differences between the two runs in terms of pressure drops and flow rates for each of the filter media.

It should be noted that the pressure drops and flow rates of the raw emulsion filtration runs were slightly higher than those of the tap water filtration runs for the anthracite and Klensorb media. The characteristics of the raw emulsion did not change after filtration, as the inlet and outlet streams were virtually identical in composition.

Table 4-9 shows the filtration results for the destabilized emulsion. Klensorb 100 appeared to be the most effective for removal of oil from the destabilized emulsion, as measured by turbidity. Using the Klensorb media, filtrate turbidity decreased to a value of 4556 NTU from the initial value of 6800 NTU for the feed emulsion, with a 0.64 cm water head loss per cm of bed. Two different sizes of anthracite (A and B) were used in order to determine the effects of filter media size on the filtration efficiency. There were no significant differences in flow rates and filtrate concentrations, but

TABLE 4-7 FILTRATION OF TAP WATER

FILTER MEDIA	FILTER WT. (g)	FLOW RATE cm/sec	PRESSURE DROP cm water/cm
SAND	310	0.146	0.16
ANTHRACITE A	150	0.143	0.15
ANTHRACITE B	150	0.138	0.35
KLENSORB100	151	0.12	0.43

TABLE 4-8 FILTRATION OF THE RAW EMULSION

FILTER MEDIA	FILTER WT. (g)	FLOW RATE cm/sec	PRESSURE DROP cm water/cm
SAND	310	0.145	0.13
ANTHRACITE A	150	0.151	0.27
ANTHRACITE B KLENSORB100	151	0.137	0.31

TABLE 4-9 FILTRATION OF THE DESTABILIZED EMULSION

FILTER MEDIA	ALUM DOSAGE mMOL/L	FLOW RATE cm/sec	PRESSURE DROP cmwater/cm	Cout/Cin
SAND	0.45	0.15	0.16	0.85
SAND	0.90	0.15	0.16	0.86
ANTHRACITE A	0.90	0.13	0.43	0.74
ANTHRACITE A	3.00	0.13	0.53	0.77
ANTHRACITE B	3.00	0.11	0.61	0.79
KLENSORB100	0.90	0.11	0.64	0.67
GLASS FIBER	3.00	0.01	0.13	0.00

Notes;

ALL MEASUREMENTS WERE CARRIED OUT AFTER 10 MINUTES OF THE FILTRATION RUN
TURBIDITY OF THE FEED EMULSION WAS 6800 NTU
PARTICLE SIZES OF THE FILTER MEDIA;
SAND : 0.81 - 1.55 mm
ANTHRACITE A : 1.02 - 1.20 mm
ANTHRACITE B : 0.6 - 0.8 mm
KLENSORB 100 : 80% > NO. 20 AND 1% < NO. 45
Cout/Cin REPRESENTS THE RATIO OF THE OUTLET TO INLET TURBIDITY

the pressure drop for the smaller media size was about 18% higher than for the larger size.

Oil recovery from the trapped oil flocs was carried out after each filtration run. About 500 mL of solvent was added to the column, and the column drained at a flow rate of 10 mL/min. The column was completely drained at the end of each filtration run. In all of the runs, the solvent was not able to dissolve and recover the trapped oil flocs. This inability was likely due to the fact that the destabilized oil droplets did not coalesce and attach onto the filter media, even though they were physically in contact with each other. It was hypothesized that the water formed a protective film around the oil droplets due to the high water content of the oil flocs, and prevented the solvent from diffusing into the oil droplet and dissolving it.

After the solvent was drained, 3 litres of tap water was fed to the bottom of the column and the oil flocs washed out. The majority of the oil flocs trapped between the filter media were recovered with the backwash flow for both the anthracite and the Klensorb filter media. The oil remaining in the sand filter media after backwash was determined to be 28 mg oil/g of sand. However, the oil remaining in the anthracite and Klensorb was determined to be about 4 mg oil/g of filter media. This result implies that the oil droplets wet the sand surface better then the hydrophobic anthracite or Klensorb surfaces. Researchers at the Wastewater Technology Centre have observed a similar phenomena; in that, bituminous oil droplets wetted sand particles better than anthracite during filtration experiments on synthetic emulsions (Averill, 1986).

4.3.3 Leaf Vacuum Filtration

In order to investigate dewatering properties of the settled oil flocs (sludge) that were obtained from a jar test, five different filter cloths were tested for their filtration performance using a standard leaf vacuum filter unit. Table 4-10 shows the types of filter cloths that were tested and a qualitative comparison of their performance. The filter cake formation was negligible and the filtrate quality was very poor for all filter cloths except PP103. In general, vacuum filtration of alum destabilized oil sludge was found to be unsatisfactory. During the filtration, the oil flocs appeared to break apart and pass through the pores of the filter cloth. This result might be due to the weak attractive forces between oil droplets.

One vacuum filtration test was conducted with alum destabilized oil sludge to which Percol 728 was added. The filtration conditions and results were given as follows:

Filter cloth	PP003
Coagulant dosage	3.0 mmol/L
Flocculant dosage	300 mg/L
Flow rate	1200 mL/min.
Applied vacuum	6.0 in Hg
Filter cake	8.0 mm Thick

The filter cake formed was as thick as 8 mm and the flow rate was 1200 mL/min. The quality of the filtered effluent was relatively good. It appeared that the polymeric flocculant formed strong bridges between the oil flocs, enabling physical entrapment of

TABLE 4-10 VACUUM FILTRATION OF THE ALUM DESTABILIZED EMULSION

FILTER CLOTH	POROSITY	FILTRATE FLOW RATE	FILTRATE QUALITY	FILTER CAKE FORMATION
NYLON 1000	HIGH	HIGH	POOR	NEGLIGIBLE
NYLON 1001	MEDIUM	HIGH	POOR	NEGLIGIBLE
PP 103	LOW	LOW	FAIR	SMALL
PP 040	MEDIUM	MEDIUM	POOR	NEGLIGIBLE
PP 003	HIGH	MEDIUM	POOR	NEGLIGIBLE

Note;

PP FILTER CLOTHS ARE HEAT CALENDERED

the flocs in the filter cloth. The water content of the oil sludge cake that formed on the surface of the filter cloth was determined to be about 50 wt%.

4.3.4 Gravity Belt Filtration

Gravity belt filtration is a process which uses horizontally mounted continuous belts to convey and dewater sludge which has been chemically conditioned. The process has economic advantages over other filtration processes (eg. vacuum filtration) as no vacuum or pressure need be applied to the filter.

The results of the tests performed at Komline-Sanderson indicate that gravity belt filtration is a promising method for treatment of the destabilized sludge. The process produced a filtrate which contained 82 mg/L of suspended solids, which constitutes a reduction of 98.9% of the solids content in the untreated emulsion. The filter cake produced contained roughly 20% by weight of oil, and is suitable for recycle to the heater treater. Analysis of the filter cake for aluminum yielded a value of 36 ppm. Additional information on gravity belt filtration is provided in Chapter 5.0.

4.3.5 Oil Recovery by Chemical Addition

The NRC-based chemical approach was not applicable for recovery of oil from the destabilized sludge. The tall oil tests produced an extremely turbid supernatant and were therefore unsuccessful. The 4-heptanone yielded a clean separation between the denser aqueous phase and the oil phase, but did not produce

coalescence of the oil. This test was also considered to be unsuccessful for this reason.

5.0 TECHNO-ECONOMIC EVALUATION

5.1 Process Flow Sheet Development

As discussed in Sections 1.1 and 2.2, the conventional process treatment train has a number of shortcomings which limit its effectiveness. The main drawbacks of the conventional process are:

i) the inability of the IGF unit to handle upset conditions due to its short retention time,

ii) frequent upsets of the sand filter unit occur due to the fluctuation in the oil content of the feed stream,

iii) operational difficulties associated with the IGF unit.

iv) high chemical costs of the sand filter unit.

Based on the experimental results obtained in this work, an alternative process has been proposed which utilizes coagulation/flocculation followed by gravity belt filtration. The process flow sheet for this alternative process is shown in Figure 5-1. The sequence of unit operations involved is described below:

i) The produced water emulsions from the free water knock-out tank (FWKT) and the heater treater (HT) are cooled to about 30°C by a plate and frame heat exchanger using the recycled treated water after deionization.

ii) The cooled emulsion stream is fed to a thickener/clarifier. Alum and Percol 728 are continuously injected into the emulsion via an in-line mixer, prior to clarification.

iii) The destabilized emulsion is settled in the thickener/clarifier unit. The clean supernatant from the

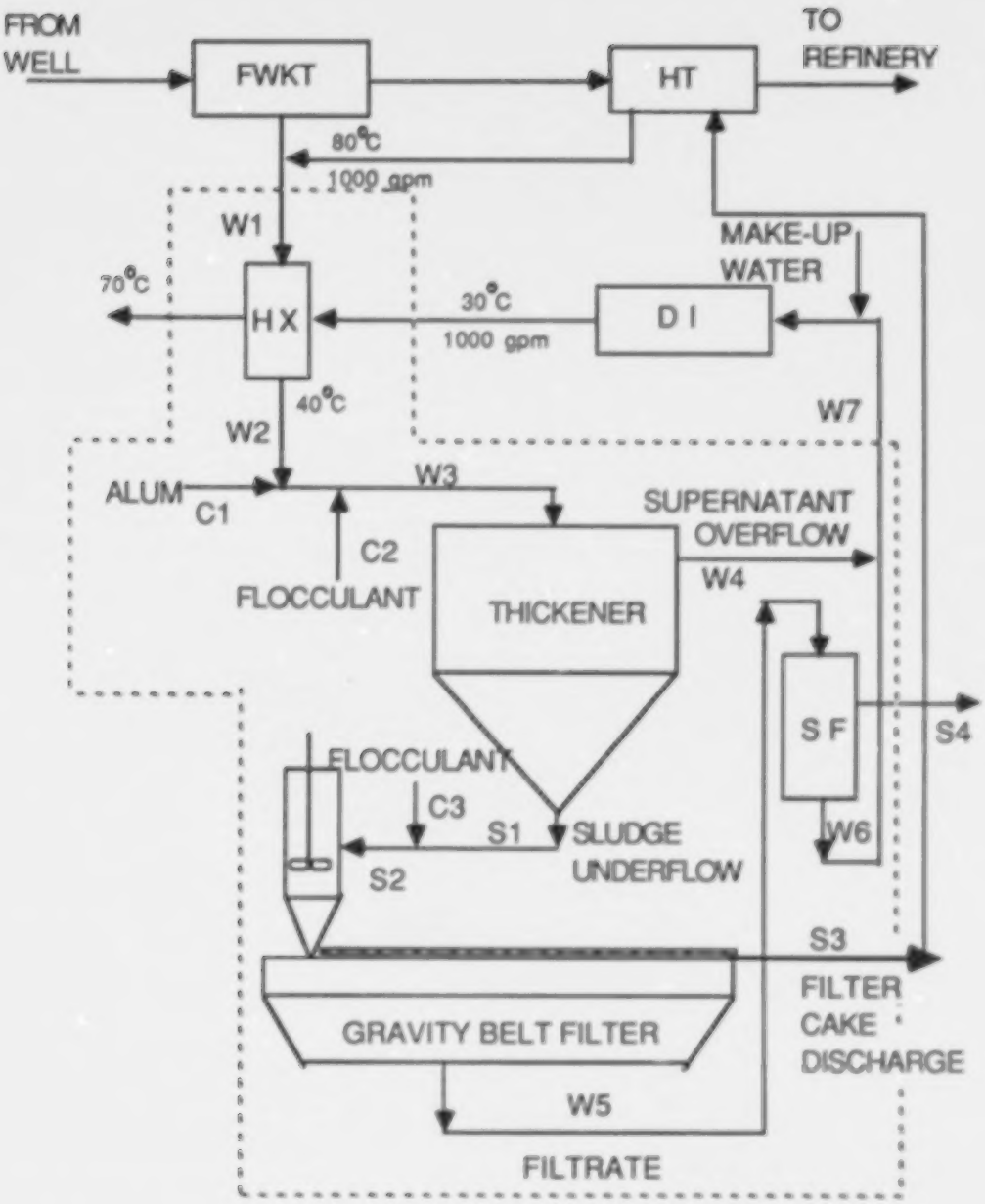


FIGURE 5-1 BATTERY LIMITS OF THE PROPOSED PRODUCED WATER TREATMENT PROCESS

thickener/clarifier is further treated by deionization steps. The oil sludge from the under flow of the unit is fed to a gravity belt filter unit with the addition of flocculant.

iv) The filtrate from the gravity belt filtration process is sent to a sand filter in order to further remove suspended oil. No additional coagulant addition is required in this step as the oil emulsion has already been destabilized. The oil filter cake containing about 80% water is suitable for recycle to the heater treater for further recovery of oil.

The advantages of the proposed process over the conventional process have been identified as follows:

i) The thickener/clarifier has a long residence time compared to the IGF and can tolerate upset conditions in feed oil levels.

ii) The quality of supernatant from the thickener/clarifier is good enough to be fed directly to hot lime softening, eliminating the need for sand filtration of roughly 75% of the total flow. As a result, significant savings in chemical costs are incurred.

iii) The frequent upset of the sand filter unit is minimized by using the relatively uniform feed quality obtained from the belt filter unit.

5.2 Cost Estimates

A conceptual cost study on the produced water treatment processes developed in this work has been carried out. This cost study is based on the results of tests that were conducted on a well head emulsion sample with a suspended oil content of approximately 7,100 mg/L. Given the early stage of development of the processes that are being considered, it would be premature to draw definitive cost estimates for commercial or semi-commercial scale facilities employing these technologies. With the information that is currently available, however, it is possible to gain some insight into the approximate relative costs of produced water treatment using the processes developed in this study.

5.2.1 Process Design Basis

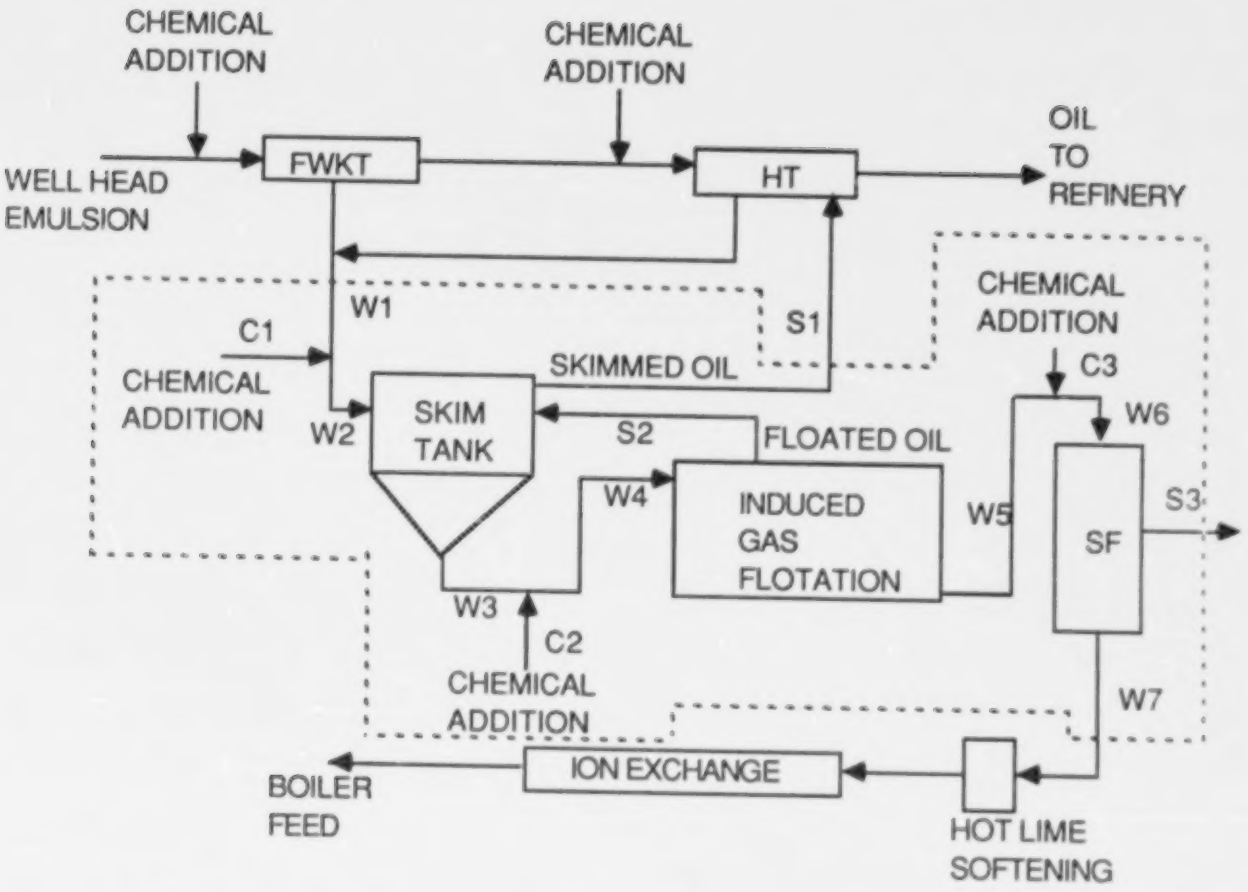
The following is a list of general assumptions and conditions that have been adopted or developed to form a basis for this cost study:

i) The produced water treatment facilities considered have been sized for approximately 1000 U.S. gal/min. of produced water.

ii) The oil concentration of the produced water is about 20000 mg/L with a pH of 8.0 and a temperature of 80°C.

iii) Battery limits of the proposed and conventional produced water treatment facilities are shown in Figures 5.1 and 5.2 respectively.

iv) All costs are reported in first quarter of 1986 Canadian dollars and the inflation factor used is M & S 793.5. The



KEY : FWKT FREE WATER KNOCKOUT TANK
HT HEATER TREATER
SF SAND FILTER

FIGURE 5-2 BATTERY LIMITS OF THE CONVENTIONAL PRODUCED WATER TREATMENT PROCESS

conversion factor used for U.S. dollars to Canadian dollars is 1.4.

v) The produced water treatment facility operates at full capacity for 330 days/year and 24 hours/day.

vi) No chemical addition to the well head emulsion prior to the free water knock-out tank is assumed.

5.2.2 Capital Cost Estimates

The capital costs have been developed based on written and verbal prices received from equipment suppliers. In some cases, the prices received were "turn-key" type estimates which included all related facilities. In other cases, the total unit costs were developed by summing up the individual equipment costs. Cost correlation tables were employed (Woods, 1983) when equipment costs were not available from suppliers.

The total capital costs were developed by using the industrial average factors at the purchase cost of main equipment in order to estimate the other direct and indirect cost of the purchased equipment. The direct cost includes shipping, installation, foundations, instruments, piping, insulation, electrical, building and structures, site preparation, and other auxiliaries. The indirect cost consists of construction fees, and contingencies. Due to the generic nature of the capital cost estimate, a 70% auxiliary cost has been added to the direct cost. This could cover items not specifically identified in the conceptual process design. The required working capital cost was not included in the total capital

cost estimated in this study. Detailed process design parameters are presented in Appendix F.

The Conventional Process

The conventional produced water treatment process consists of three main unit operations; skim tank, induced gas flotation, and granular filtration as shown in Figure 5-2. Battery limits of this process are indicated as dotted lines in Figure 5-2. The produced water feed to the battery limit comes from a storage tank in which the produced waters generated from the free water knock-out tank (FWKT) and the heater treater (HT) are collected. The flows leaving the battery limits are as follows; skimmed oil flow from the skimmed oil collection tank, treated water flow from the sand filter, and sand filter back-wash water flow. The costs for pumping the skimmed oil from the skimmed oil collection tank to the heater treater and the treatment cost for the sand filter back-wash water were not included in the cost estimation, as they are beyond the battery limits.

A list of detailed equipment purchase costs for the conventional process is presented in Table 5-1. The cost of a skim tank having 10 hours of retention time was estimated from cost correlation data (Woods, 1983). The cost of an IGF unit which has four minutes of fluid residence time was obtained from Wemco. The cost of a sand filter which has a total of 250 ft^2 of surface area with 4 gpm/ft^2 of hydraulic loading was obtained from Eimco. The details of design parameters of the individual units are presented in Appendix F.

TABLE 5-1 DETAILED CAPITAL COSTS OF CONVENTIONAL PROCESS

SYSTEM	EQUIPMENT	NUMBER	SIZE	COST
Skim Tank Unit	Skim Tank	1	600000gal	$189,990
	Oil Collection Tank	1	6250gal	$19,460
	Chemical Storage Tank	1	50gal	$1,000
	Feed Pump	1	20Hp	$4,000
	Chemical Feed Pump	1	0.25Hp	$1,000
	Under Flow Pump	1	20Hp	$3,000
			TOTAL	$218,450
IGF Unit	IGF including accessary	1		$180,000
	Float Recovery Tank	1	400gal	$8,200
	Chemical Storage Tank	1	50gal	$1,000
	Storage Tank	1	60000gal	$40,700
	Feed Pump	1	20Hp	$3,000
	Chemical feed Pump	1	0.25HP	$1,000
	Float Oil Pump	1	5Hp	$2,000
			Total	$235,900
Sand Filter Unit	Sand Filter(with back wash)	1	250ft2	$80,000
	Storage Tank	1	57000gal	$39,500
	Chemical Storage Tank	1	1000gal	$2,000
	Feed Pump	1	20Hp	$3,000
	Chemical Feed Pump	1	0.25Hp	$1,000
			Total	$125,500
Total Equipment Purchase Cost			$579,850	

The total capital cost of the conventional process is presented in Table 5-2. The total capital cost is $2,592,000, consisting of $1,798,000 of direct cost and $794,000 of indirect expenses.

The Proposed Process

The proposed produced water treatment process consists of four main unit operations; heat exchanger, thickener/clarifier, gravity belt filter, and granular filtration. Battery limits of this process is shown as dotted lines in Figure 5-1. The produced water feed to the battery limit comes from a storage tank in which the produced waters generated from the FWKT and the HT are collected. The flows leaving the battery limit are; recovered oil filter cake from the gravity belt filter, treated water from the thickener/clarifier overflow, and the sand filter effluent and back-wash water. Treatment cost of sand filter back-wash water and transportation costs of recovered oil filter cake were not included in this cost estimate. The cooling water used in the heat exchanger unit was assumed to be available after the treated water and make-up water goes through a deionization process. Due to the nature of the proposed treatment processes developed in this work, the design parameters of thickener/clarifier and gravity belt filter were obtained from laboratory bench scale experiments. The cost of a heat exchanger unit having 548 m^2 of heat transfer area was obtained from ITT. The cost of a thickener/clarifier unit which were sized based on settling properties of the produced water in the presence of optimum coagulant and flocculant dosage was provided by Dorr-Oliver. The cost of two

TABLE 5-2 TOTAL CAPITAL COST OF CONVENTIONAL PRODUCED WATER TREATMENT PROCESS

Purchase Cost of Equipment	$579,850		
Shipping Charges	$57,985		
Installation of Equipment	$156,560		
Foundations	$75,381		
Instruments	$86,978		
Piping	$144,963		
Insulation	$75,381		
Electrical	$52,187		
Building and Structures	$104,373		
Site Preparation	$57,985		
Auxiliaries	$405,895		
TOTAL DIRECT COSTS		$1,797,538	
Construction and Field Expenses	$237,739		
Engineering Expenses	$191,351		
Contractors Fees	$121,769		
Contingencies	$243,537		
TOTAL INDIRECT EXPENSES		$794,396	
TOTAL COSTS			$2,591,934

gravity belt filters having 6.0 m^2 of surface area each was provided by Komline-Sanderson which conducted bench scale filtration runs with the samples provided by ZENON in order to obtain design parameters. The cost of a sand filter having 62.5 ft^2 of surface area was obtained from Eimco. A list of detailed equipment purchase costs is presented in Table 5-3. It should be noted that the cost of the thickener/ clarifier unit is almost half of the total equipment purchase cost. The total capital cost of the proposed process is presented in Table 5-4. The total capital cost is $2,315,000 consisting of $1,605,000 of direct cost and $710,000 of indirect expenses.

5.2.3 Operating Cost Estimates

The operating costs have been developed based on chemical, labour and maintenance, and energy requirements. The data on required chemical dosage for the processes were obtained either from laboratory experiments or were estimates provided by current chemical suppliers to the oil industry. The energy required for the processes was estimated by summing up the energy requirements of individual process components. The maintenance cost was set based on 5% of the total base equipment cost and a contingency based on 10% of other operating costs. The contingency has been added to cover items not specifically identified in the operating cost estimates.

It was assumed that the plant would operate at full capacity of 1000 gpm for 330 days/year, 24 hours/day. This would allow for some down time (scheduled or unscheduled) and allow for periods where the plant would not operate at full scale.

TABLE 5-3 DETAILED EQUIPMENT PURCHASE COSTS OF PROPOSED PROCESS

SYSTEM	EQUIPMENT	NUMBER	SIZE	COST
Heat Exchange Unit	P/F Heat Exchanger	1	548m2	$56,000
	Feed Pump	1	20Hp	$4,000
			Total	$60,000
Thickener/ Clarifier Unit	Thickener/Clarifier (including mechanism)	1	6000ft2	$187,500
	Chemical Storage Tank	3	100gal	$7,000
	Storage Tank	1	60000gal	$40,700
	Chemical Feed Pump	3	0.25Hp	$4,000
	Sludge Pump(under flow)	1	15Hp	$5,000
			Total	$244,200
Sand Filter	Sand Filter(with back wash)	1	62.5ft2	$50,000
	Storage Tank	1	15000gal	$25,800
	Feed Pump	1	15Hp	$3,000
			Total	$78,800
Gravity Belt Unit	Belt Filter(with hopper)	2	12m2	$90,000
	Storage Tank	1	15000gal	$25,800
	Chemical Storage Tank	1	3600gal	$17,100
	Chemical Feed Pump	1	0.5Hp	$2,000
			Total	$134,900
Total Equipment Purchase Cost				$517,900

TABLE 5-4 TOTAL CAPITAL COSTS OF PROPOSED PRODUCED WATER TREATMENT PROCESS

Equipment Purchase Cost	$517,900		
Shipping Charges	$51,790		
Installation of Equipment	$139,833		
Foundations	$67,327		
Instruments	$77,685		
Piping	$129,475		
Insulation	$67,327		
Electrical	$46,611		
Building and Structures	$93,222		
Site preparation	$51,790		
Auxiliaries	$362,530		
TOTAL DIRECT COSTS		$1,605,490	
Construction and Field Expenses	$212,339		
Engineering Expenses	$170,907		
Contractors Fees	$108,759		
Contingencies	$217,518		
TOTAL INDIRECT EXPENSES		$709,523	
TOTAL COSTS			$2,315,013

The following list summarizes the unit costs considered in the operating cost estimates:

i) Electrical Power : 1.35 cents/kw

ii) Operator Labour (including benefits) : $135/day, 365 days/yr

iii) Chemicals:

a) Demulsifier : $13.25/gal

b) Coagulants (polyelectrolyte) : $22.71/gal

c) Flocculant : $13.25/gal

d) Alum : $0.30/kg

e) Percol 728 : $3.95/kg

A breakdown of total yearly operating costs of the conventional produced water treatment is presented in Table 5-5. The costs of chemicals and labour represent more than 80% of the total operating cost. The energy cost is not significant, representing less than 5% of the total operating cost. It should be noted that the chemical dosage of the sand filter unit is relatively large, resulting in high chemical cost.

In Table 5-6, a breakdown of the total yearly operating cost of the proposed produced water treatment process is presented. The labour cost consists of more than 50% of the total operating cost. The chemical cost of the proposed process is significantly lower than that of the conventional process, mainly because of eliminating the chemical cost for the sand filter in the conventional process.

TABLE 5-5 CONVENTIONAL PRODUCED WATER TREATMENT PROCESS: YEARLY OPERATING COSTS

MATERIALS (Chemicals)		
Skim Tank (10 ppm @ $13.13/gal.)		$62,370
IGF (5 ppm @ $22.50/gal.)		$52,391
Sand Filter (25 ppm @ $13.13/gal.)		$152,775
Total		$267,536
LABOUR		
Operators		
3 shifts/day	3	
1 swing	1	
1 supervisor	1	
Total	5	
(total 5 operators, @$135/day, 365 days/yr.)		$246,375
ENERGY		
Skim Tank (40.25 HP)		
IGF (85.75 HP)		
Sand Filter (20.25 HP)		
(146.25 HP X 0.7457 X 24 X 330 X 1.35 cents/KW)		$29,700
MAINTENANCE		
5% of total base equipment cost		$28,993
CONTINGENCIES		
Other Operating Expenses (10 % of other expenses)		$48,124
TOTAL OPERATING COSTS		$620,728

TABLE 5-6 PROPOSED PRODUCED WATER TREATMENT PROCESS: YEARLY OPERATING COSTS

MATERIALS	**(Chemicals)**		
	Thickener/Clarifier		$54,103
	Gravity belt filter (50 ppm @ $3.95/kg)		$87,986
			$142,089
LABOUR			
Operators			
	3 shifts/day	3	
	1 swing	1	
	1 supervisor	1	
	Total	5	
	(total 5 operators @$135/day, 365 days/yr.)		$246,375
ENERGY			
	Heat exchanger(20HP)		
	Thickener/Clarifier (23.75 HP)		
	Gravity belt filter (5.5 HP)		
	Sand Filter (15 HP)		
	(64.25 HP X 0.7457 X 24 X 330 X 1.35 cents/KW)		$13,053
MAINTENANCE			
	5% of total base equipment cost		$25,895
CONTINGENCIES			
	Other Operating Expenses		
	(10 % of other expenses)		$37,331
TOTAL OPERATING COSTS			$464,743

5.3 Cost Comparison of the Two Processes

In order to determine the cost benefits of the proposed produced water treatment process, an overall cost comparison of the two processes is presented in Table 5-7. The capital cost of the proposed process is about 10% less than that of the conventional one primarily due to the elimination of the IGF unit in the proposed process. The operating cost of the conventional process is more than 20% higher than that of the proposed one mainly because of high chemical cost for the sand filter unit. The yearly costs were calculated on the basis of 11% amortization for 5 years. The yearly cost of the proposed process is more than 17% less than that of the conventional one. The treatment costs of 1000 U.S. gal/min of produced water are $2.78 for the conventional process and $2.29 for the proposed one. For an average size produced water treatment system, this translates into an annual savings of approximately $230,000. Even though the cost estimates provided in this study are only intended to be used for preliminary evaluation of alternatives and should not be used for budgetary purposes, the overall cost of the produced water treatment process proposed in this work is approximately 17% less than that of the conventional process.

TABLE 5-7 COST COMPARISON OF THE CONVENTIONAL AND PROPOSED PROCESSES

COSTS	CONVENTIONAL PROCESS	PROPOSED PROCESS
CAPITAL COST	$2,592,000	$2,315,000
OPERATING COST	$621,000	$465,000
YEARLY COST*	$1,321,000	$1,090,000
$/1000 GAL TREATED	$2.78	$2.29

Note;
* 11% amortization for 5 years

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APPENDIX A

ANALYTICAL PROCEDURES

ANALYTICAL PROCEDURES

pH

The pH was determined using an Extech Model 651 digital meter (Extech, Boston, Mass.) following the method described in the operating manual.

Conductivity

The conductivity was determined using a YSI Model 32 Conductance meter (Scientific Division, Yellow Springs Instrument Co., Inc.) following the method described in the operating manual.

Turbidity

The turbidity of the samples was determined using an HF Instruments Model DRT 100 Turbidimeter as per the instruction manual.

Total Suspended Oil (TSO) and Total Suspended Solids (TSS)

i) Filter known volume (V) of sample through a washed, ashed, and preweighed (W_1) 0.45 micron glass fiber filter.

ii) Dry filter overnight at 100°C

iii) Weigh filter (W_2).

iv) Ash filter. Care must be taken to increase temperature slowly from 150°C to 450°C to volatilize oil without burning. Muffle for 1 hour at 450°C.

v) Weigh filter (W_3)

vi) Calculations:

$$TSO = \frac{W_2 - W_3}{V} \qquad TSS = \frac{W_2 - W_1}{V}$$

Note: Weight loss at 100°C assumed to be only water - along with water loss there may be a loss of the low-boiling components of the oil - resulting in a low TSO value.

Total Dissolved Solids (TDS) and Total Dissolved Oil (TDO)

i) Weigh crucible (W_1).

ii) Transfer all filtrate from TSS + TSO determination of known volume (V) to crucible.

iii) Dry crucible overnight at 60°C, dessicate, and weigh (W_2).

iv) Ash residual in crucible. Muffle for 1 hour at 450°C.

v) Dessicate and weigh crucible (W_3).

vi) Calculations:

$$TDS = \frac{W_2 - W_1}{V} \qquad TDO = \frac{W_2 - W_3}{V}$$

Alkalinity

Alkalinity was determined following the procedure described in AWWA Standard Methods 403.

Filtered Organic Carbon (FOC)

i) Filter samples through a prewashed 0.45 micron glass fiber filter.

ii) The TOC was determined using a Beckman Model 915 TOC analyzer (Beckman Instruments, Inc., Fullerton, California) following the method described in the operating manual.

Organic Acids

The emulsion sample was prepared by back extraction to isolate the acid fraction only before analysis by gas chromatography. The pH of the sample was adjusted to 3 with HCl and was then extracted with dichloromethane. The organic phase was then back extracted with aqueous potassium hydroxide. The aqueous base extract containing salts of organic acids was then reacidified and extracted with dichloromethane to yield the acid fraction in an organic phase. The organic phase was evaporated down before GC analysis. Figure A-1 shows a summary of the isolation procedure used.

A portion of the isolated fraction was then injected into a Hewlett-Packard 5880A gas chromatograph with flame ionization detection for determination of the concentration of water insoluble organic acids.

Anion Scan (IC)

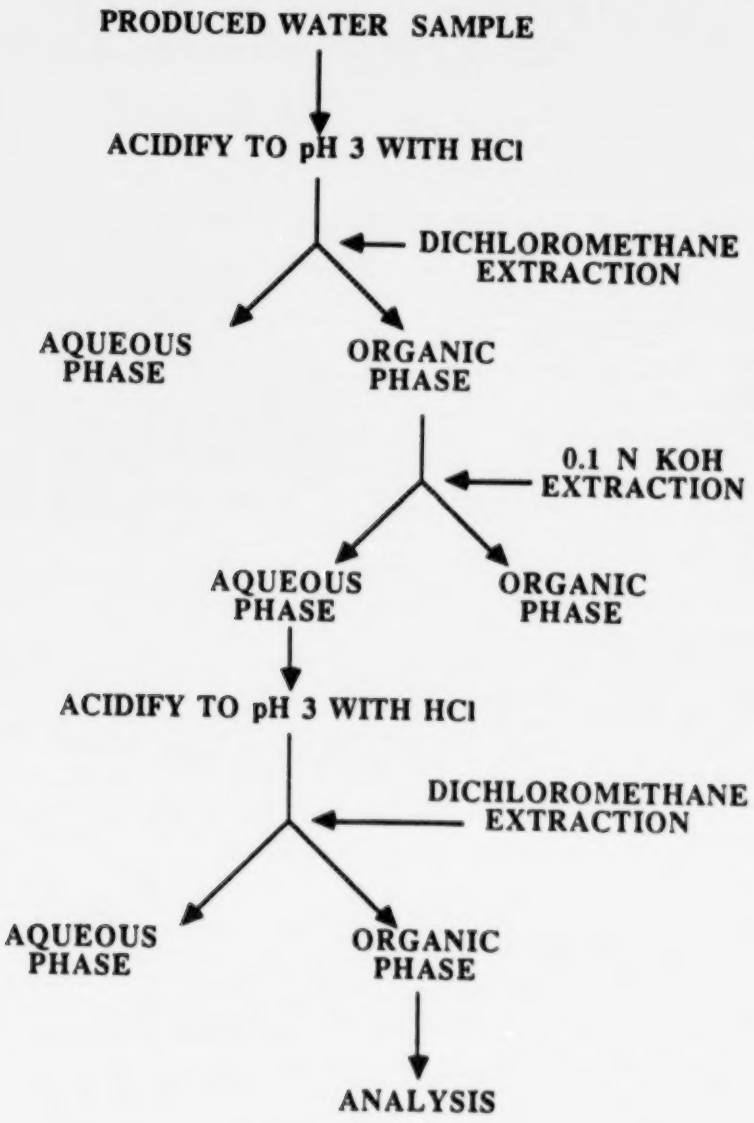
Samples were analyzed using Ion Chromatography for Cl, PO_4, SO_4, NO_3, NO_2, and F. Results were reported in mg/L.

Cation Scan (ICAP)

The samples were analyzed by inductively coupled argon plasma for Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, V, and Zn. Results were reported in mg/L.

FIGURE A - 1

PREPARATION OF PRODUCED WATER SAMPLES FOR GC ANALYSIS



Calculated Hardness

Hardness was calculated by multiplying the concentrations of Ca and Mg obtained in the cation scan by the appropriate factor to obtain equivalent calcium carbonate, and by summing these $CaCO_3$ concentrations. To obtain the $CaCO_3$ equivalent (mg/L) of Ca and Mg, the concentrations were multiplied by 2.5 and 4.116 respectively.

Titration Curve

The alkalinity of the emulsion was determined by titrating with 0.1 N HCl. The procedure that was followed is described below:

i) 100 mL of emulsion was added to a 250 mL beaker.

ii) The sample was placed on a magnetic stirrer and mixed to ensure homogeneity. The pH of the sample was taken after equilibrium was established.

iii) The titrant was added to the emulsion in increments of 0.2 mL. After each addition, the pH of the emulsion was taken and recorded, along with the volume of titrant added.

iv) The addition of titrant was continued until a solution pH of 2 was obtained.

APPENDIX B

PROCEDURES USED IN COAGULANT PREPARATION

APPENDIX B

PROCEDURES USED IN COAGULANT PREPARATION

Alum

166.5 g of $Al_2(SO_4)_3 \cdot 18H_2O$ was weighed and dissolved in 1 litre of ultrapure water to make up a solution which was 0.5 M in the Al^{3+} ion. The solution was stored in a polyethylene bottle until needed.

Ferric Chloride

67.5 g of $FeCl_3 \cdot 6H_2O$ was weighed and dissolved in 1 litre of ultrapure water, to make up a solution which was 0.25 M in the Fe^{3+} ion. During the dissolution, yellow foam formed at the surface of the solution; this foam disappeared when the dissolution was complete. Total time required for dissolution was approximately one hour. The solution was stored in a polyethylene bottle until needed.

Prepolymerized Aluminum

The solution that was used as a prepolymerized aluminum coagulant was derived from a commercially available product called SternPAC. The SternPAC product was diluted with ultrapure water to yield a solution that was 0.5 M in the Al^{3+} ion. The solution was stored in a polyethylene bottle until needed.

Prepolymerized Iron

a) 13.5 g of $FeCl_3 \cdot 6H_2O$ was weighed and dissolved in 100 mL of ultrapure water to yield a 0.50 M solution in the Fe^{3+} ion.

The 0.50 M $FeCl_3 \cdot 6H_2O$ solution was transferred to a 500 mL Erlenmeyer flask.

b) 110 mL of 1N NaOH was added to a separate flask and diluted with ultrapure water to a total volume of 200 mL.

c) The ferric chloride solution was neutralized by dropwise addition of the diluted NaOH solution, to obtain a OH/Fe ratio of 2.2:1.

d) Ultrapure water was added to the neutralized solution to bring the total volume to 500 mL. The solution was used for jar testing within 20 hours of preparation, so as to prevent appreciable change. The resultant solution was 0.10 M in the Fe^{3+} ion.

APPENDIX C

PROCEDURES USED IN JAR TESTS

APPENDIX C

PROCEDURES USED IN JAR TESTS

The jar tests were conducted on a Phipps & Bird Jar Tester. The procedure used was as follows:

i) Six 1 litre jars containing the oil-in-water emulsion were prepared. Five of these jars were to be used to test dosage levels, the sixth was used as a blank.

ii) To five of the jars, sodium hydroxide was added for adjustment of pH. The amount of sodium hydroxide was determined by performing preliminary titrations on samples to which coagulant had been added.

iii) The six jars were placed under the paddles of the jar test apparatus, and the paddles were lowered into the emulsion samples. The apparatus was turned on and the mixing rate set to 90 rpm. The samples were mixed for 30 seconds at this speed in order to ensure homogeneity.

iv) After the initial mixing, the coagulant was added to each of the five test jars. The time of coagulant addition was designated as time t = 0. Mixing of the destabilized samples proceeded at 90 rpm for a period of one minute.

v) At the end of the one minute fast mix period, the stir rate was reduced to 30 rpm. Stirring at this rate proceeded for a total of five minutes.

vi) At the end of the five minute period, stirring of the samples was discontinued. The paddles were carefully

withdrawn from the jars so as not to disturb the flocs which had formed.

vii) Each of the jars were monitored for floc formation and settling rate. After no further settling had occurred, the sludge height was measured and used to calculate final sludge volume as a percentage of the initial sample volume.

viii) Samples of the jar test supernatant were withdrawn, taking care so as not to disturb the settled sludge layer. The samples were analyzed for pH, conductivity, and turbidity, as well as other parameters for assessment of boiler feedwater quality.

APPENDIX D

PROCEDURES USED IN FILTRATION EXPERIMENTS

APPENDIX D

PROCEDURES USED IN FILTRATION EXPERIMENTS

A) Granular Media Filtration

A series of filtration experiments were conducted to determine the potential of granular media filtration for recovery of oil from a destabilized oil-in-water emulsion. These experiments were conducted in both batch and recycle modes, and included runs on tap water and untreated emulsion for reference purposes. The three media types investigated were sand, anthracite, and Klensorb 100 (a mixture of anthracite and resin). The media sizes tested were as follows:

a) Sand : 0.81 to 1.55 mm

b) Anthracite : i) 1.02 to 1.2 mm

ii) 0.60 to 0.80 mm

c) Klensorb : 80% > 0.84 mm

A schematic of the filtration apparatus that was used is shown in Figure D-1. A summary of the protocols is given below.

Filtration of Tap Water

i) About 400 g of filter media was weighed into a 500 mL beaker and poured into the filter column to a depth of 7.5 cm. The weight of filter media added was obtained by subtracting the weight of the sand remaining in the beaker from the total original weight. The column was tapped gently to ensure that the filter media was evenly distributed.

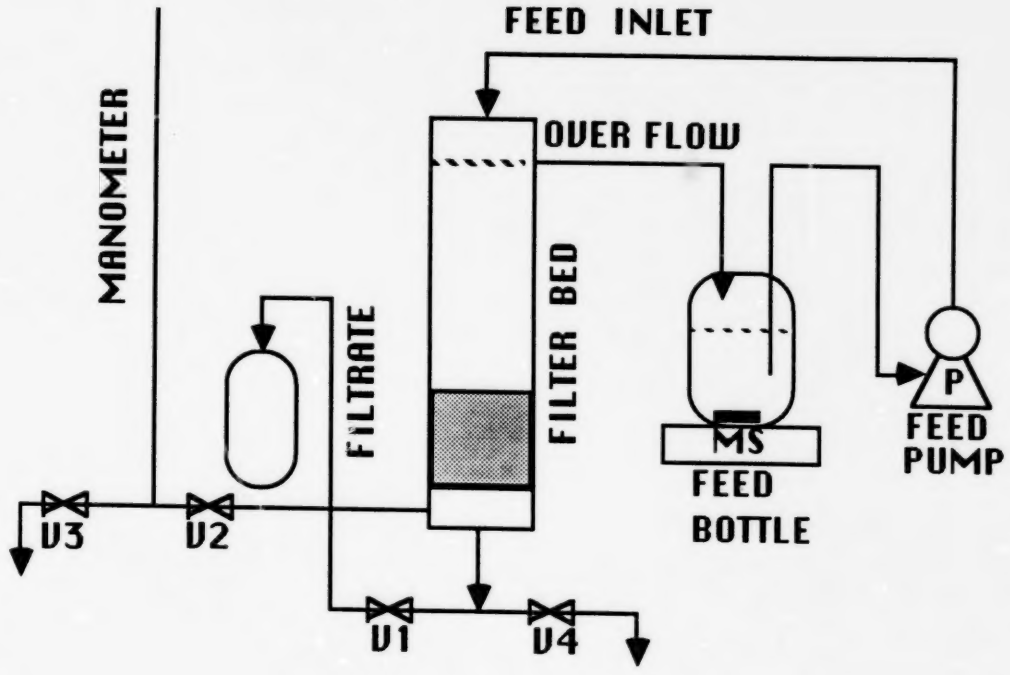


FIGURE D-1 SCHEMATIC FLOW SHEET OF FILTRATION EXPERIMENTAL SET UP.

ii) The filter unit was assembled in the up-flow mode. Water up-flow was initiated to suspend the filter media to a depth of approximately 10 cm (about 30% by volume).

iii) The up-flow rate was slowly reduced and the column gently tapped as the filter media settled. The water up-flow was then stopped.

iv) The filter unit was changed to the down-flow mode and the water flow started with the valve V_2 open. After a run of about one minute, the valve V_1 was closed and the water flow stopped. At this point, the water level in the manometer was recorded.

v) At time t = 0, the water flow was started and the valve V_1 was opened.

vi) For a period of one hour, the water flow rate and the pressure drop were measured every five minutes.

Filtration of Oil-in-Water Emulsion

i) The steps (i) to (iii) of tap water filtration were repeated.

ii) The filter unit was placed in the down-flow mode and the water drained from the column by opening valve V_4 until the water level reached a distance of about 2 cm above the filter media. Valve V_4 was then closed and the emulsion flow initiated.

iii) When the emulsion overflowed the column, the valves V_1 and V_2 were opened. Time t = 0 was designated as the time at which all clean water had left the column.

iv) The test runs were conducted for a thirty minute period. During the tests, filtration flow rate, pressure drop, and filtrate turbidity were monitored every five minutes.

Filtration of Destabilized Oil-in-Water Emulsion

i) A three litre sample of the emulsion was prepared and placed in the feed bottle.

ii) The steps (i) to (iii) of tap water filtration were repeated.

iii) The filter unit was placed in the down-flow mode and the water drained from the column by opening valve V_4 until the water level reached a distance of about 2 cm above the filter media. Valve V_4 was then closed.

iv) The required dosages of coagulant and sodium hydroxide were added to the emulsion, while mixing the emulsion with a magnetic stirrer. The conditions selected for destabilization were based on the results of the jar tests.

v) The emulsion flow was initiated. When the emulsion overflowed the column, the valves V_1 and V_2 were opened. Time t = 0 was set at the point when all of the clean water had left the column.

vi) The test runs were conducted for a period of thirty minutes. During this time, the runs were monitored for filtrate flow rate, pressure drop, and filtrate turbidity.

Filtration of Destabilized Oil-in-Water Emulsion with Recycle of Filtrate

i) Repeat steps (i) to (vi) as given in "Filtration of Destabilized Oil-in-Water Emulsion", with the exception that the filtrate is returned to the emulsion reservoir.

ii) The runs in the recycle mode were conducted for a maximum period of 1.5 hours, or until no further changes in the pressure drop had occurred. During the tests, filtrate flow rate, pressure drop, and filtrate turbidity were monitored every five minutes.

B) **Glass Fiber Bed Filtration**

The glass fiber bed filtration experiment was conducted on an emulsion sample which had been previously destabilized with 3.0 mmol/L of alum as the aluminum ion. The experiment was carried out on the apparatus shown in Figure D-1. The procedure is described below.

i) 30.4 g of glass fiber was weighed and packed into the bottom of the column, to a depth of 7.5 cm.

ii) The filtration experiment was carried out as described in steps (ii) to (vi) as given in "Filtration of Destabilized Oil-in-Water Emulsion".

iii) When the pressure drop stabilized, the filtration was stopped and the emulsion drained from the bed.

C) **Leaf Vacuum Filtration**

A series of tests were conducted to determine the potential of vacuum filtration for treatment of the sludge generated by

destabilization of the emulsion. This test was carried out by generating sludge in a jar test, and separating the supernatant from the sludge. The vacuum filtration experiments were then carried out on samples of the sludge, using commercial filter cloths of varying composition and porosity. The procedure used during the tests is described below.

Sample Preparation

i) Four litres of alum destabilized sludge were prepared. The conditions chosen for destabilization were determined from the jar test results.

ii) The supernatant from the jar test was decanted from the settled sludge.

iii) Approximately 500 mL of the sludge was added to a 800 mL beaker. This sample was used in the experiment described below in Part C.

Calibration of the Test Unit

i) The test unit was assembled as shown in Figure D-2. Approximately 500 mL of tap water was placed in the beaker.

ii) A 20 inch Hg vacuum was applied to the tap water sample. The amount of filtrate collected in the graduated funnel was monitored every 20 seconds for a period of four minutes. At the end of this time, a reading of the vacuum gauge was taken to determine if the pressure had changed significantly during the course of the experiment.

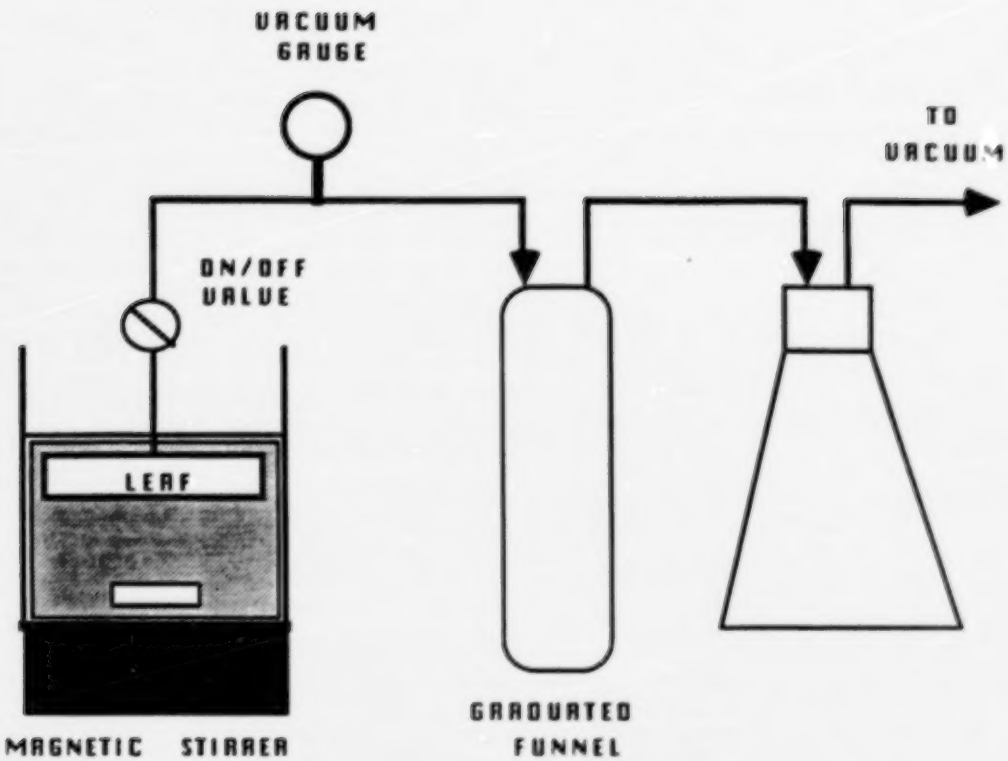


FIGURE D-2 SCHEMATIC FLOW SHEET OF THE VACUUM LEAF TEST UNIT

iii) At the end of the four minute interval, the leaf was taken out with the vacuum still on and held upside down for a further four minute period. At the end of the second four minute period, the vacuum was stopped.

Leaf Test with Destabilized Sludge

i) The test unit was assembled as shown in Figure D-2. The feed sludge was generated as described in Part A above. The sludge was gently mixed by use of the magnetic stirrer.

ii) A 20 inch Hg vacuum was applied to the sludge sample. The amount of filtrate collected in the graduated funnel was monitored every 20 seconds for a period of four minutes. The change in vacuum was also recorded.

iii) At the end of the four minute interval, the leaf was taken out with the vacuum still on and held upside down for another four minutes. Then the vacuum was stopped. During this period, the filtrate rate was recorded at one minute intervals.

iv) The approximate thickness of the filter cake was measured. The filter cake was then removed from the filter cloth by use of a razor blade.

v) The weight of the wet filter cake was measured. The wet filter cake was dried at room temperature to constant weight. The weight of the dry filter cake was measured, and subtracted from that of the wet filter cake to determine moisture loss.

vi) The collected filtrate was analyzed for pH, conductivity, and turbidity.

D) **Gravity Belt Filtration**

The potential of gravity belt filtration for treatment of the destabilized sludge was evaluated at Komline-Sanderson Ltd. Samples of an alum (0.45 mmol/L as Al^{3+})/Percol 728 (1 mg/L) destabilized sludge were forwarded to Komline-Sanderson. Komline added 50 mg/L of Percol 728 to the sludge prior to filtration. The filtration rates that were obtained were used to size a full scale gravity belt filtration system for treatment of destabilized sludge. A sample of the filtrate obtained during the test was obtained and analyzed for suspended solids.

APPENDIX E

PROCEDURES USED IN OIL RECOVERY EXPERIMENTS

APPENDIX E

PROCEDURES USED IN OIL RECOVERY EXPERIMENTS

A number of techniques were evaluated to determine their potential for recovering oil from the destabilized flocs after filtration, or from the destabilized sludge. These techniques included water backwash, solvent extraction, and chemical addition. The procedures that were employed are as follows.

Backwash of Filter Media

After the granular media filtration tests were conducted, backwash of the filter media was attempted for recovery of oil. Two types of backwash fluids were used, water and mineral spirits. The procedure used for backwashing is given below.

i) When the filtration run was completed, the pump was stopped and the emulsion in the column drained to a point just above the filter media. This was accomplished by opening valve V_4 while valves V_1 and V_2 were closed.

ii) The filter unit was placed in the up-flow mode. Three litres of either tap water or solvent were placed in the feed bottle and pumped through the filter media to backwash the media. The effluent was collected for analysis of suspended solids.

iii) After backwashing, the filter media was removed from the column and dried at room temperature to constant weight.

iv) The weight of the filter media was measured and subtracted from the initial weight to determine the weight gain or loss of the filter media.

Backwash of Glass Fibre Packed Column

After the glass fibre bed filtration experiment, mineral spirits was used to backwash the bed to recover oil. The procedure that was used is as follows.

i) After the emulsion was drained from the filter bed, the solvent was added up to the overflow line in the bed.

ii) The draining solvent was collected and the flowrate measured. The oil content in the solvent was determined by measuring the weight of product before and after air drying. The difference in weight was that of the recovered oil.

iii) After solvent extraction of the oil, the glass fiber was removed from the column and air dried to constant weight. The final weight was measured and compared with the initial weight that had been charged to the column.

Chemical Addition

Two sets of tests using tall oil and 4-heptanone were conducted to determine the applicability of the NRC-based chemical approach for recovery of oil from the destabilized sludge. The background information relevant to this approach is given in Section 2.4. The procedure used is described below.

i) Approximately 600 mL of sludge was prepared from the emulsion using 0.45 mmol/L of alum and 1 ppm of Percol 728.

The sludge was divided into 6 100 mL samples and poured into 150 mL hypo-vials (THM bottles).

ii) The sludge samples were placed in an oven and heated to a temperature of 80°C.

iii) When the temperature reached 80°C, tall oil and 4-heptanone were added to the beakers, at the following dosages: 1 wt.%, 5 wt.%, and 10 wt.%.

iv) The samples were shaken vigorously for a period of ten minutes to dissolve the added chemicals. The samples were then stored in the oven at 90°C for 24 hours.

v) At the end of this period, the samples were withdrawn from the oven, and observations recorded.

Solvent Extraction of Filter Cake

Solvent extraction using mineral spirits was evaluated for recovery of oil from the filter cake. Filter cake produced from the leaf vacuum experiments was dissolved in the solvent to determine its solubility properties.

APPENDIX F

DESIGN PARAMETERS FOR THE CONVENTIONAL AND PROPOSED PROCESSES

DESIGN PARAMETERS FOR THE CONVENTIONAL PROCESS

1. **Skim Tank System**

   a) Skim Tank

flow rate:	1000 U.S. gpm
retention time:	10 hours
tank size:	600,000 gal
chemical dosage:	10 ppm @ $13.25/gal.

   b) Skimmed Oil Collection Tank

flow rate:	52 U.S. gpm
retention time:	2 hours
tank size:	6240 gal.

   c) Chemical Storage Tank

chemical dosage:	10 ppm
retention time:	24 hours
tank size:	50 gal.

2. **IGF System**

   a) IGF Unit (Wemco #84)

flow rate:	1000 U.S. gpm
retention time:	4 minutes

   b) Float Recovery Tank

tank size:	10% of IGF (400 gal)

   c) Chemical Storage Tank

chemical dosage:	5 ppm
retention time:	24 hours

	tank size:	50 gal.
d)	Storage Tank	
	flow rate:	1000 U.S. gpm
	retention time:	1 hour
	tank size:	60,000 gal.

3. **Sand Filter System**

a)	Sand Filter	
	flow rate:	1000 U.S. gpm
	hydraulic loading:	4 U.S. gpm/ft^2
	total surface area:	250 ft^2
	column diameter:	18 ft
	filter media:	dual media (sand and anthracite)
	backwash:	15 U.S. gpm/ft^2 for 5 min. (50% sand, 100% anthracite expansion)
	includes backwash system	
b)	Chemical Storage Tank	
	tank size:	100 gal.
	retention time:	24 hours
c)	Storage Tank	
	tank size:	57,000 gal.

DESIGN PARAMETERS FOR THE PROPOSED PROCESS

1. **Heat Exchanger System**

   a) Heat Exchanger (Model E150 ITT)

flow rate:	100 U.S. gpm
overall heat transfer coefficient:	2900 Btu/hr.ft^2
total heat transfer area:	548 m^2

   b) Feed Pump (Model 1510-6CB ITT)

flow rate:	1000 U.S. gpm with 50 ft water head

2. **Thickener/Clarifier System**

   a) Thichener/Clarifier (Dorr-Oliver)

flow rate:	1000 U.S. gpm
total surface area:	6000 ft^2
under flow rate:	0.9 ft/hr.
residence time:	approx. 45 min.

   b) Storage Tank

flow rate:	1000 U.S. gpm
retention time:	1 hour
tank size:	60,000 gal.

   c) Alum Storage Tank: 400 gal. with 24 hours of retention time

   d) Flocculant Storage Tank: 300 gal. with 24 hours of retention time

e) NaOH Storage Tank: 50 gal. with 24 hours of retention time

3. **Sand Filter System**

a) Sand Filter Unit (Eimco)

flow rate:	250 U.S. gpm
hydraulic loading:	4 U.S. gpm/ft^2
column diameter:	9.0 ft
backwash:	at 15 U.S. gpm/ft^2 for 5 min.
filter media:	dual (sand and anthracite)

b) Storage Tank

flow rate:	250 U.S. gpm
tank size:	15000 gal.

4. **Gravity Belt Filter System**

a) Gravity Belt Filter (Komline-Sanderson)

filter size:	12.0 m^2

b) Flocculant Storage Tank With Agitator

chemical dosage:	50 ppm with 0.5% solution
retention time:	24 hours
tank size:	3600 gal.

APPENDIX G

KEY PERSONNEL AND ORGANIZATIONS CONTACTED

ORGANIZATION	INDIVIDUAL(S) CONTACTED
Allied Colloids Toronto, Ontario	Mr. J. Gagen (416) 793-9473
A.O.S.T.R.A. Edmonton, Alberta	Dr. T. Cyr (403) 427-7623
Baker Oil Treating Calgary, Alberta	Mr. L. Scarpino (403) 279-8959
Delta Projects Calgary, Alberta	Mr. G. Page (403) 259-0411
Dorr-Oliver Inc. Orillia, Ontario	Mr. D. Forman Mr. R. Auster (705) 325-6181
Eimco Oakville, Ontario	Mr. T. Matthews (416) 625-6070
ITT Fluid Products Canada Guelph, Ontario	Mr. T. Ward (519) 821-1900
Komline-Sanderson Ltd. Brampton, Ontario	Mr. J.E. Bindon Mr. A. Bowser (416) 453-5330

Saskatchewan Research Council	Mr. R. Ranganathan
Regina, Saskatchewan	Dr. F. Mourits
	Mr. L. Kurusz
	(306) 787-9332
Universal Filter Media	Mr. R. Green
Markham, Ontario	(416) 898-7741
Wastewater Technology Center	Dr. A. Zaidi
Burlington, Ontario	Mr. D. Averill
	Mr. D. Vachon
	(416) 637-4558
Wemco Canada	Mr. W. Sullivan
Mississauga, Ontario	(416) 625-1637

DESCRIPTION OF CONTACTS MADE

CONTACT: Mr. J. Gagen

AFFILIATION: Allied Colloids

Toronto, Ontario

(416) 793-9473

Mr. J. Gagen was contacted to get quotes on the cost for purchasing Percol 728.

CONTACT: Dr. T. Cyr

AFFILITATION: A.O.S.T.R.A.

Edmonton, Alberta

(403) 427-7623

Dr. T. Cyr was contacted during the literature survey segment of the project to obtain information on research conducted on produced water treatment.

CONTACT: Mr. L. Scarpino

AFFILIATION: Baker Oil Treating

Calgary, Alberta

(403) 279-8959

Mr. L. Scarpino was contacted to get costs for chemicals used in the produced water treatment process.

CONTACT: Mr. G. Page

AFFILIATION: Delta Projects

Calgary, Alberta

(403) 259-0411

Mr. G. Page was contacted to gain additional information on the conventional produced water treatment process.

CONTACTS: Mr. D. Forman
Mr. R. Auster
AFFILIATION: Dorr-Oliver Inc.
Orillia, Ontario
(705) 325-6181

Dorr-Oliver personnel were contacted to get quotes for a thickener/clarifier unit.

CONTACT: Mr. T. Matthews
AFFILIATION: Eimco
Oakville, Ontario
(416) 625-6070

Mr. T. Matthews was contacted to get a quote for a full scale sand filter unit.

CONTACT: Mr. T. Ward
AFFILIATION: ITT Fluid Products Canada
Guelph, Ontario
(519) 821-1900

Mr. T. Ward was approached in order to get a quotation for a plate and frame heat exchanger and ancillary equipment.

CONTACTS: Mr. J.E. Bindon
Mr. A. Bowser
AFFILIATION: Komline-Sanderson Ltd.

Brampton, Ontario

(416) 453-5330

Komline-Sanderson personnel were contacted to aid in the evaluation of both vacuum and gravity belt filtration for produced water treatment. Komline-Sanderson provided full scale system costs for two gravity belt filters.

CONTACTS: Mr. R. Ranganathan

Dr. F. Mourits

Mr. L. Kurusz

AFFILIATION: Saskatchewan Research Council

Regina, Saskatchewan

(306) 787-9332

Saskatchewan Research Council personnel were contacted during the literature survey portion of the project to obtain information on produced water characteristics and treatment methods. SRC provided ZENON with analytical data on emulsions from the Meota project, and was instrumental in procuring the emulsion sample that was used in the test program.

CONTACT: Mr. R. Green

AFFILIATION: Universal Filter Media

Markham, Ontario

(416) 898-7741

Mr. R. Green was contacted to obtain samples of filter cloth which were used to evaluate the potential of vacuum filtration for produced water treatment.

CONTACTS: Dr. A. Zaidi

Mr. D. Averill

Mr. D. Vachon

AFFILIATION: Wastewater Technology Center

Burlington, Ontario

(416) 637-4558

Wastewater Technology Center personnel were contacted during the literature survey portion of the project, in order to obtain information on:

1) produced water characteristics
2) coagulation of produced water
3) filtration of produced water

CONTACT: Mr. W. Sullivan

AFFILIATION: Wemco Canada

Mississauga, Ontario

(416) 625-1637

Mr. W. Sullivan was contacted to get a quote for a full scale induced gas flotation unit.